# Wavelength Controlled Synthesis and Degradation of Thermoplastic Elastomers Based on Intrinsically Photoresponsive Phenylvinylketone

Nethmi De Alwis Watuthanthrige,[1] Jennifer A. Reeves,[1] Madison T. Dolan, [1] Shah Valloppilly, [2] Mehdi B. Zanjani,[3] Zhijiang Ye,[3] Dominik Konkolewicz[1,*]

[1] Department of Chemistry and Biochemistry, Miami University, 651 E High St, Oxford OH, 45056, USA

[2] Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, Nebraska 68588, USA

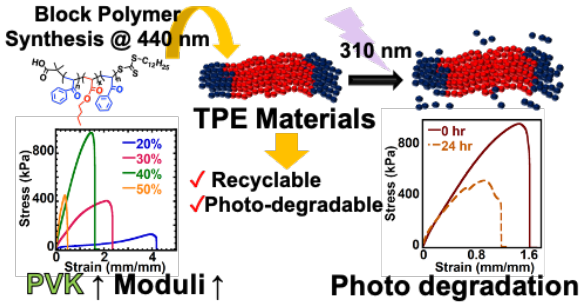
[3] Department of Mechanical and Manufacturing Engineering, Miami University, 650 E High St, Oxford, OH 45056, USA

*Corresponding Author: d.konkolewicz@miamiOH.edu

## Abstract

Phenyl vinyl ketone (PVK) is known for its responsiveness to light, with initiation promoted under visible light and degradation of poly(PVK) promoted under UV radiation. Thus, expensive radical sources such as photocatalysts and initiators can be substituted by PVK to promote intrinsic photoinitiation giving well-defined polymers. Block copolymers polymer are readily prepared by reversible deactivation radical polymerization techniques, this study is the first approach of formation block polymers through the intrinsically generated radicals of PVK monomers, where the monomer serves as both the chain forming unit and the radical source. In this work, the photoinitiation of PVK was used to generate poly(PVK) homopolymers, which were chain extended with butyl acrylate (BA) and PVK to synthesize poly(PVK-BA-PVK) block polymers. The structural differences of PVK and BA caused microphase separation of the block segments to form thermoplastic elastomers (TPEs) with interesting thermomechanical properties. Due to the differences in glass transition temperature, the poly(PVK) blocks formed the hard

segments of the TPE, with the poly(BA) segments forming the soft elastic domains. The TPE materials could achieve a maximum of 1000 kPa stress, and 400% strain at break. Irradiation of the TPE materials with 310 nm UV light promoted the degradation of poly(PVK) segments, with associated changes decrease in mechanical strength and elasticity. Molecular dynamic simulations confirmed the trends observed in TPE mechanical properties with the changes in polymer composition. Further, the simulations provided the atomistic insight to the underlined degradation mechanism of PVK in block polymers and its effect on TPE mechanical properties.




## Introduction

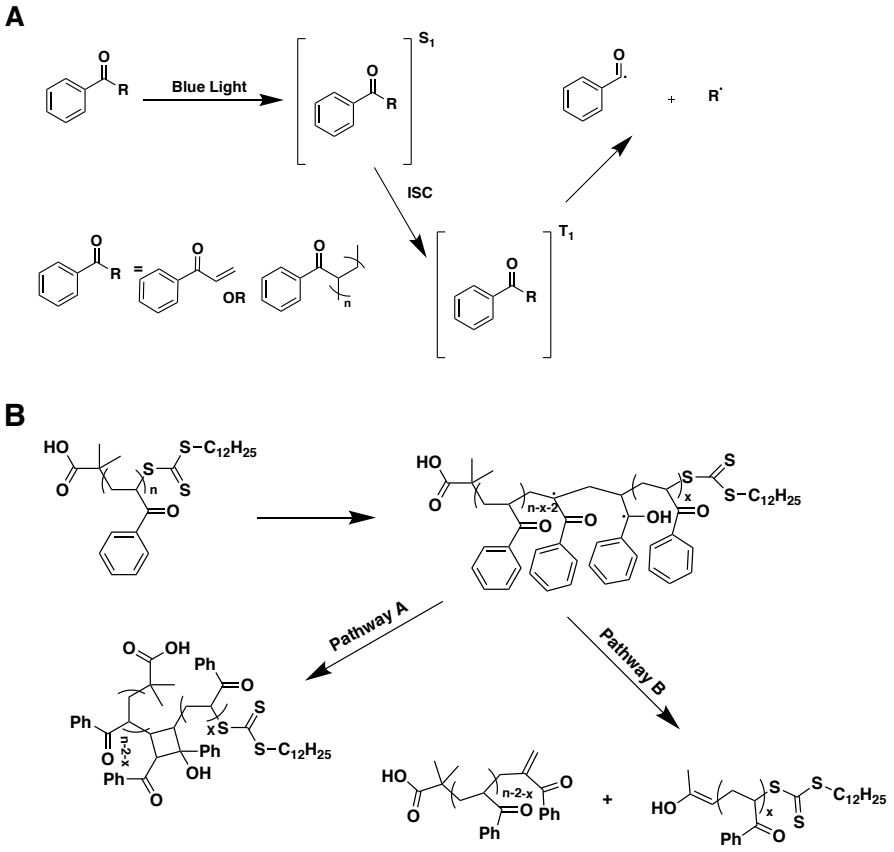
Thermoplastic elastomers (TPEs) possess both thermoplastic and elastomeric properties.[1,2] TPE materials are commercially produced using techniques such as melt extrusion.[3] These materials are segmented with "hard" and "soft" block segments in a block copolymer.[4] Typically, a polymer block with a low glass transition temperature ($T_g$) behaves as a soft rubbery matrix and is connected to a physically crosslinked glassy hard domain to form a reversibly crosslinked polymer network.[1] Owing to the microphase separations of these block copolymers, TPEs have melt and flow behavior at elevated temperature, yet cool down to form solid rubber-like materials. The proportions of the soft and hard blocks alter the thermoplastic and elastomeric characteristics of TPEs, enabling their properties to be tuned to, any applications.[4,5,6] Commonly tri- or multi-

block co-polymers are employed in TPE materials (ABA triblock, ABC triblock or $(AB)_n$ multiblock).[7]

Plastics and polymer based materials have long lifetimes within the environment. The long degradation time of many synthetic polymers has caused major environmental concerns.[8,9,10] To fulfill the growing demand for synthetic polymer materials, many industries are considering substituting traditional polymers for newer degradable materials. Bio- and photo-degradable polymer are viable alternatives to traditional plastics for preparing self-degrading materials.[11,12,13] The toughness of TPE materials primarily comes from the glassy hard domains.[4,14] Thus, incorporation of a degradable hard block segment into a segmented tri block polymer is an effective way of preparing degradable TPEs.[15,16,17] Since, sunlight contains a broad spectrum of electromagnetic radiation ranging from UV to radio waves,[18] self-degradation of polymers could occur if the material absorbs sunlight to trigger chain-scission, potentially reducing the polymer waste from the environment.

Phenyl vinyl ketone (PVK) belongs to the vinyl ketone subgroup of molecules and it is known that their homopolymers poly(PVK) could undergo photodegradation under UV radiation.[19,20,21] Recently we have discovered that PVK monomer and homopolymers are not only capable of photo-degradation under UV light, but these polymers also undergo self-initiated photopolymerization under blue light.[22,23] Through these primary studies, we obtained well-defined homopolymers of PVK with low dispersities (Đ of 1.1 to 1.2). Butyl acrylate (BA) forms polymers with a low glass transition temperature, forming a soft matrix at room temperature. Combining PVK and BA monomers in a ABA type block polymer poly(PVK-BA-PVK) could provide the typical soft-hard block characteristics of TPE materials, with photodegradability from the PVK blocks. Different strategies  such as reversible addition-fragmentation chain transfer

(RAFT) and atom transfer radical polymerization (ATRP) techniques, have been used to synthesize tri- and multi- block polymers.[24,25,20] In this study, we prepared TPE materials based on poly(PVK-BA-PVK) block polymers using PVK self-initiated photo-polymerization under blue light. Due to the poly(PVK) units these polymers could be degraded under 310 nm UV irradiation. The proposed mechanism for PVK photoinitiation through a Norrish Type I process is shown in Scheme 1A, and the proposed degradation through a Norrish type II process is given in Scheme 1B.




Scheme 1: (A) Proposed Norrish type 1 mechanism for the initiation of radical propagation under blue light (B) Proposed Norrish type 2 mechanism for the degradation process of poly(PVK) under 310 nm UV light [23]

## Results and Discussion

ABA type block polymers were synthesized using PVK and BA to form TPE materials with the polyPVK units forming the hard glassy domains in the A blocks and the poly(BA) forming the soft domain in the B block. The polymerization was performed under blue light using the self-initiated photopolymerization of PVK in the presence of (isobutyric acid)yl dodecyl trithiocarbonate (iBADTC) as the chain transfer agent. The initial PVK block was then chain extended with BA and finally PVK, respectively, to obtain an ABA type triblock copolymer. This photo-responsive intrinsic radical formation approach has never been used to synthesize block polymers and subsequent TPE material formation. Our previous work showed that the iniferter effect is negligible on the PVK photopolymerization, indicating the radical generation occurs mostly through PVK monomer and not from the RAFT agent.[23] Notably, even after the first block of PVK is formed, a small amount of PVK can still dissociate into radicals and initiate subsequent chain extension. Final chain extension is given upon the addition of an additional amount of PVK. Each chain extension was run to at least 95% conversion of the PVK or BA monomer. This PVK initiated triblock copolymer synthesis is described in Figure 1a.

To study the effect of chain length and monomer composition on mechanical properties of TPEs, three different chain lengths and five different compositions (Table 1) of hard (PVK) and soft (BA) segments were evaluated. Typically, well-defined, predominantly monomodal block polymers were obtained. The narrow distribution of these long polymer chains further justifies that only a small portion of PVK radicals at the chain ends participate in the chain extension process while others remain unaffected with the blue light. With the polymer with a higher PVK fraction in the tri-block polymers, a small amount of dead chains were observed, presumably due to their termination and participation in the visible light promoted radical generation reactions. Using a

peak deconvolution approach, the $M_n$ of each segment was calculated for the ABA triblock copolymers and is given in Table S2, and for the AB block copolymers in Table S3. The successful chain extension is expected by each chain extension reaching at least 95% conversion, with a significant major peak, with a molecular weight consistent with the expected molecular weight of the complex block copolymer. The small amounts of low molecular weight homopolymers found by deconvolution should not impact microphase separation of block copolymers.[26] Well defined block copolymers with efficient chain extensions were confirmed by size exclusion chromatography (SEC) as indicated in Figure 1b.

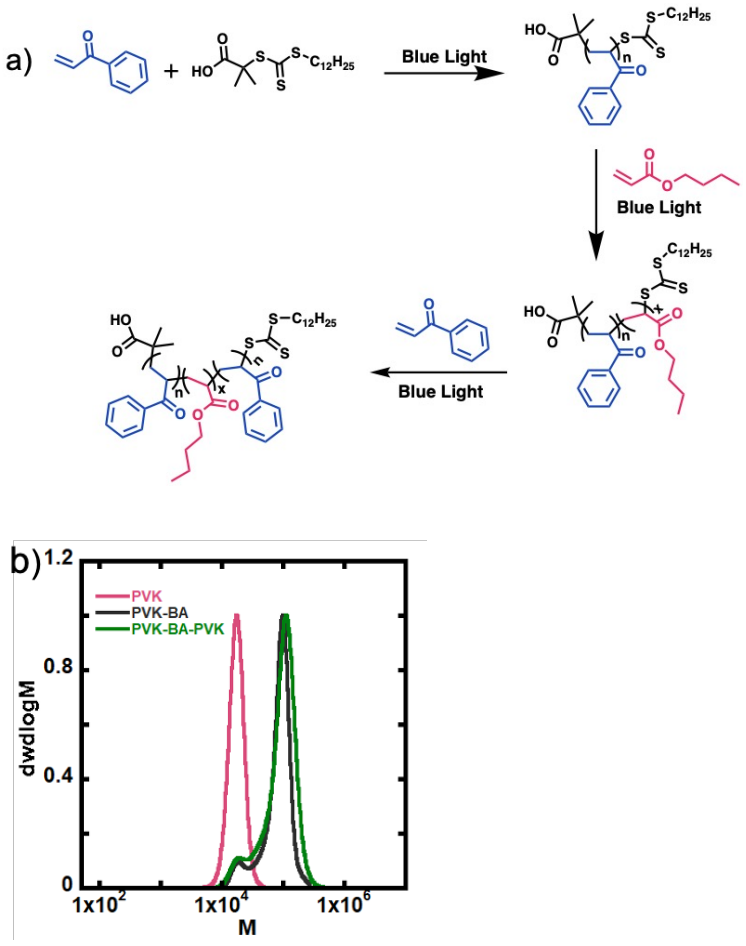



Figure 1: a). Schematic representation of the synthesis of PVK-BA-PVK $A_nB_xA_n$ type tri-block polymer b). MW distribution for three blocks in SEC traces in $PVK_{150}$-$BA_{450}$-$PVK_{150}$ (DP 750, 40% PVK) block polymer where the A units correspond to PVK and the B units correspond to BA.

The mechanical properties of these tri-block TPE polymer materials were studied. The TPE polymers were molded in to dog-bone shaped materials with the slow evaporation of the solvent. Materials were characterized through, SEC, nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), infrared spectroscopy (IR), small-angle X-ray scattering (SAXS) analysis, tensile testing and shear rheology. Photodegradation induced changes in these materials were studied using tensile testing and SEC analysis.

Table 1: Composition, $M_n$, $M_w$, and Đ values of $A_1BA_2$ type thermoplastic polymers with three different chain lengths and five different PVK percentages. *Mn, Mw, and Đ values were calculated through deconvolution of SEC data (as described in SI) obtained with RI detector and THF as the eluent at 30 °C.

| Chain length | PVK (%) | $A_1BA_2$ Composition | $A_1$ block | | | $A_1B$ block | | | $A_1BA_2$ block | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $M_n$ (kDa) | $M_w$ (kDa) | Đ | $M_n$ (kDa) | $M_w$ (kDa) | Đ | $M_n$ (kDa) | $M_w$ (kDa) | Đ |
| 500 | 20 | $PVK_{50}$-$BA_{400}$-$PVK_{50}$ | 5.1 | 5.7 | 1.1 | 56 | 59 | 1.1* | 68 | 72 | 1.1* |
| 750 | 20 | $PVK_{75}$-$BA_{600}$-$PVK_{75}$ | 7.0 | 8.2 | 1.2 | 80 | 105 | 1.3* | 99 | 112 | 1.1* |
| 1000 | 20 | $PVK_{100}$-$BA_{800}$-$PVK_{100}$ | 11 | 12 | 1.1 | 111 | 121 | 1.1* | 132 | 142 | 1.1* |
| 750 | 10 | $PVK_{37.5}$-$BA_{675}$-$PVK_{37.5}$ | 3.4 | 3.8 | 1.1 | 93 | 98 | 1.1* | 97 | 102 | 1.1* |
| 750 | 30 | $PVK_{112.5}$-$BA_{525}$-$PVK_{112.5}$ | 11 | 13 | 1.2 | 75 | 83 | 1.1* | 99 | 111 | 1.1* |
| 750 | 40 | $PVK_{150}$-$BA_{450}$-$PVK_{150}$ | 17 | 18 | 1.1 | 78 | 84 | 1.1* | 97 | 108 | 1.1* |
| 750 | 50 | $PVK_{187.5}$-$BA_{375}$-$PVK_{187.5}$ | 17 | 21 | 1.2 | 67 | 74 | 1.1* | 98 | 115 | 1.2* |

## Mechanical Properties

The soft and hard blocks of TPEs contribute to the elastomeric and thermoplastic properties, respectively. Many styrene containing block copolymers have been employed as TPEs in several applications.[27,28,29,30] PVK is structurally similar to styrene due to the aromatic benzene ring in its structure. In styrene-based TPEs, π-π stacking between aromatic components supports forming reversible physical crosslinking in a soft matrix to hold the material together.[27] Similarly, the presence of PVK units in block polymers could introduce π-π stacking, and hard rigid chain segments, to enhance the mechanical strength of TPE materials.[31] Hence, we anticipate that the stiffness of these materials are governed by the fraction of PVK as in styrene based thermoplastic

elastomers. Upon increasing the PVK percentage, the fraction of hard block segments increases within the TPE materials. As expected, with the increment of the PVK fraction (20% to 50%) in block polymer, tensile strength of these materials increased (Figure 2a). Materials with a higher percentage of PVK tend to have higher young's modulus but lower strain at break ($\varepsilon_{break}$). Tensile strength ($\sigma_{peak}$) and $\varepsilon_{break}$ can be correlated with the fraction of the hard block segments and as well as the chain entanglements. While the tensile strength increases with the fraction of hard block segments and chain entanglements, the strain at break was increased with chain entanglements promoted at higher chain lengths in soft BA matrix promoted at higher chain length, but decreased with the fraction of hard blocks from PVK.[27]

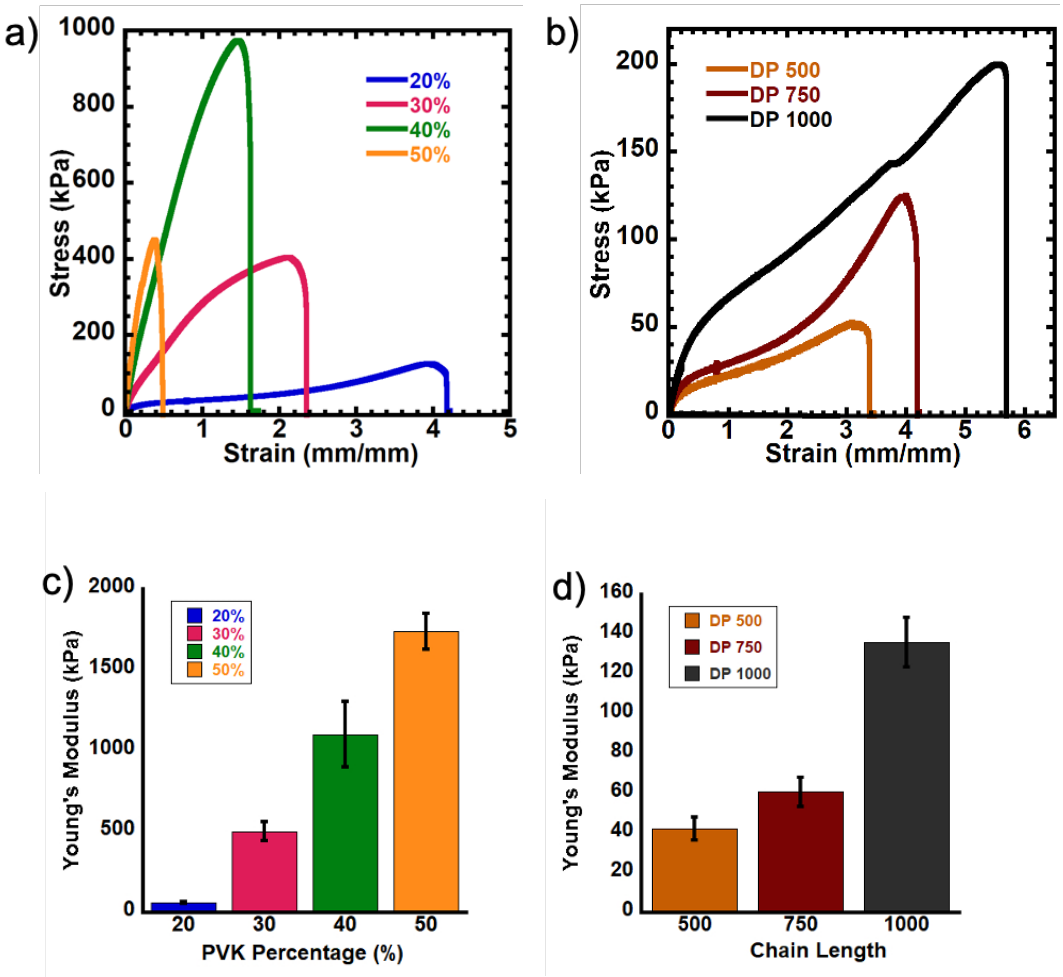


Figure 2: Tensile testing data for a). Different chain lengths: $PVK_{50}$-$BA_{400}$-$PVK_{50}$ (DP 500), $PVK_{75}$-$BA_{600}$-$PVK_{75}$ (DP 750) and $PVK_{100}$-$BA_{800}$-$PVK_{100}$ (DP1000), b). Different PVK percentage: PVK $PVK_{75}$-$BA_{600}$-$PVK_{75}$ (20% PVK), $PVK_{112.5}$-$BA_{525}$-$PVK_{112.5}$ (30% PVK) , $PVK_{150}$-$BA_{450}$-$PVK_{150}$ (40% PVK), $PVK_{187.5}$-$BA_{375}$-$PVK_{187.5}$ (50% PVK). c). Bar charts for young's modulus variation (calculated using Ogden hyper-elastic constitutive law)[32] with different PVK percentages (20%-50%) at DP 750, d) Bar charts for young's modulus variation (calculated using Ogden hyper-elastic constitutive law)[32] with different chain lengths (DP 500 to 1000) at 20% PVK.

The Flory-Huggins thermodynamic interaction parameter ($\chi$), and the number of repeating units (N) plays a vital role in the preparation of TPEs.[33,34] The choice of monomers determines the $\chi$ parameter for each TPE materials hence their microphase separation behavior as well. However, the quantification of the $\chi$ parameter is beyond the scope of this work. To hold the material together a strong association of hard domains in a soft elastic matrix is needed, and weak microphase separation would cause the collapse of the specific shape of the material or cause the material to flow. For the PVK and BA based triblock copolymers, we observed viscous liquid materials below 20% PVK content implying the necessity of the critical amount of the PVK blocks to induce phase separation and hold the polymer network together. As implied in literature, hard block fractions shorter than the critical length correspond to microphase separation tend to disperse within the soft segments and longer hard block segments aggregate within the soft segment.[35,36,37] Furthermore, the addition of more repeating units (N) to the block polymers increases the chain entanglements as well as the thermodynamic drive for phase separation within the TPE materials.[38] More entanglements result a close packing of each phase and contribute to an entropic loss by reducing the movement within the phases.[39] Subsequently, an enhancement in stress and strain value for the materials was observed with more longer chain lengths (Table 2, Figure 2b). We attribute the

higher strain to the larger number of entanglements, with the higher stress likely due to stronger phase separations causing a higher effective number of crosslinks, as well as a greater number of entanglements. Both introduction of hard more hard block segments and chain units enhanced the overall young's modulus of these materials (Figure 2c).

In typical block polymers, the polymer segments are connected with each other through chemical linkages. As Leiber described, due to the incompatibility between chosen monomers, the two blocks phase separate from each-others.[39] As a result of this, these blocks tend to segregate and form thermodynamically favored micro phase-separated structures.[40,41] Due to the chemical linkages between blocks, they cannot phase separate to a mixture of two homo-polymers, yet the block copolymers still display the properties of each individual polymer segments due to the microphase separations. Microphase separation can be evidenced through two distinguishable glass transition temperature ($T_g$) values for each block in DSC analysis.[42] As expected, distinct $T_g$ values have not appeared for the materials with lower PVK percentages (less than 20%). This suggests that block copolymers with less than 20% PVK do not show a considerable microphase separation and are incapable of holding the material together into a TPE. Materials with higher PVK fractions displayed $T_g$s around 80 °C and -50 °C, which agrees with the $T_g$s of PVK and BA homopolymers respectively (Table 2, Figure S1).[43,44,45,46] In addition, PVK-BA-PVK materials exhibited some characteristic SAXS features to confirm their microphase separations. However the acquired SAXS data were not sufficiently well-resolved to evaluate the phase-separated morphologies (Figure S7, and S8). Elastomeric properties and transition temperatures of these TPE materials were revealed through rheological data. (Figure 3, Figure S9). As Wittenberg et al. suggested some TPE materials can display a noticeable tanδ maxima even exceeding their actual $T_g$s due to the specific non-covalent interactions they possess.[47] In our TPE materials, the peak in

tanδ which exceeds the $T_g$ of the hard block could come from the non-covalent interactions associated with the PVK molecules (Figure S10).

Table 2: Maximum stress ($\sigma_{peak}$), Strain at break ($\varepsilon_{break}$), and Observed glass transition temperatures for BA and PVK ($T_g$ (BA) and $T_g$ (PVK)) of ABA type thermoplastic polymers with three different chain lengths and five different PVK percentages. *Errors represent a standard error based on 4 measurements

| **Chain length** | **PVK (%)** | **$A_nB_xA_n$ Composition** | $\sigma_{peak}$ (kPa) | $\varepsilon_{break}$ (mm/mm) | $T_g$ (BA) (°C) | $T_g$ (PVK) (°C) |
|---|---|---|---|---|---|---|
| 500 | 20 | $PVK_{50}$-$BA_{400}$-$PVK_{50}$ | 50 ± 10 | 3.3± 0.2 | -42 | - |
| 750 | 20 | $PVK_{75}$-$BA_{600}$-$PVK_{75}$ | 110±10 | 4.2± 0.2 | -44 | - |
| 1000 | 20 | $PVK_{100}$-$BA_{800}$-$PVK_{100}$ | 200± 10 | 5.8± 0.2 | -45 | - |
| 750 | 10 | $PVK_{37.5}$-$BA_{675}$-$PVK_{37.5}$ | - | - | -41 | - |
| 750 | 30 | $PVK_{112.5}$-$BA_{525}$-$PVK_{112.5}$ | 400± 20 | 2.1± 0.2 | -43 | - |
| 750 | 40 | $PVK_{150}$-$BA_{450}$-$PVK_{150}$ | 940± 60 | 1.7± 0.1 | -45 | 80 |
| 750 | 50 | $PVK_{187.5}$-$BA_{375}$-$PVK_{187.5}$ | 570± 40 | 0.7± 0.1 | -42 | 81 |

**Reprocessability**

Unlike the thermoset materials, thermoplastic materials can be reprocessed into different shapes upon melting or dissolving in an appropriate solvent.[48,49] Raising the temperature above the $T_g$ of both blocks can enable the free movements of polymer chains at elevated temperature and slow cooling process permits block polymers to adopt phase separation patterns to facilitate the transformation to the new shape.[4] Alternatively, solvents can facilitate reprocessing by allowing the polymers to flow. To demonstrate the reprocessability, poly(PVK-BA-PVK) TPE materials were sliced into small pieces, dissolved in dioxane, and transformed into dog bone shapes upon slow evaporation of the solvent. The mechanical properties of the reprocessed materials were compared with the original materials. Both the materials had similar stress values while the reprocessed materials had slightly lower strain at break than original material (Figure S15). The loss of elastomeric properties (strain) could be attributed to the chain scission of the BA matrix during the reprocessing protocol.[50]

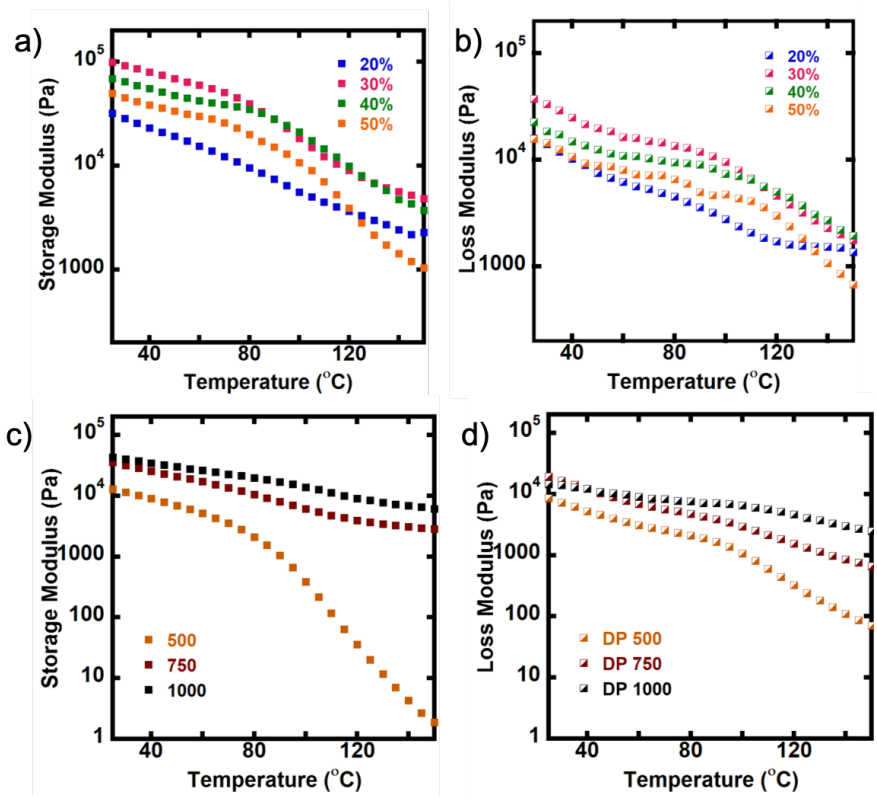
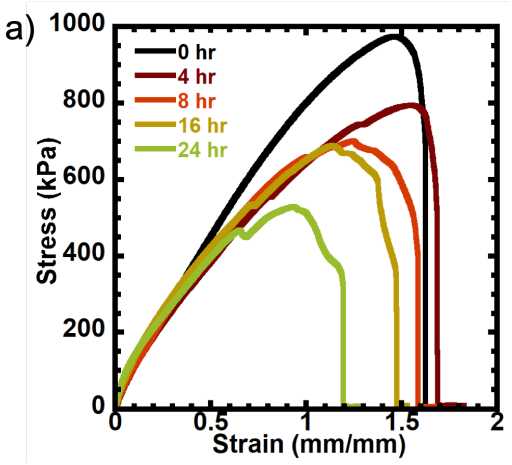



Figure 3: Rheological temperature sweep plots for the TPE materials a) Storage modulus variation for the TPE materials with 10%-50% PVK percentages. b) Loss modulus variation for the TPE materials with 10%-50% PVK percentages. c) Storage modulus variation for the TPE materials with different lengths. d) Loss modulus variation for the TPE materials with different lengths.



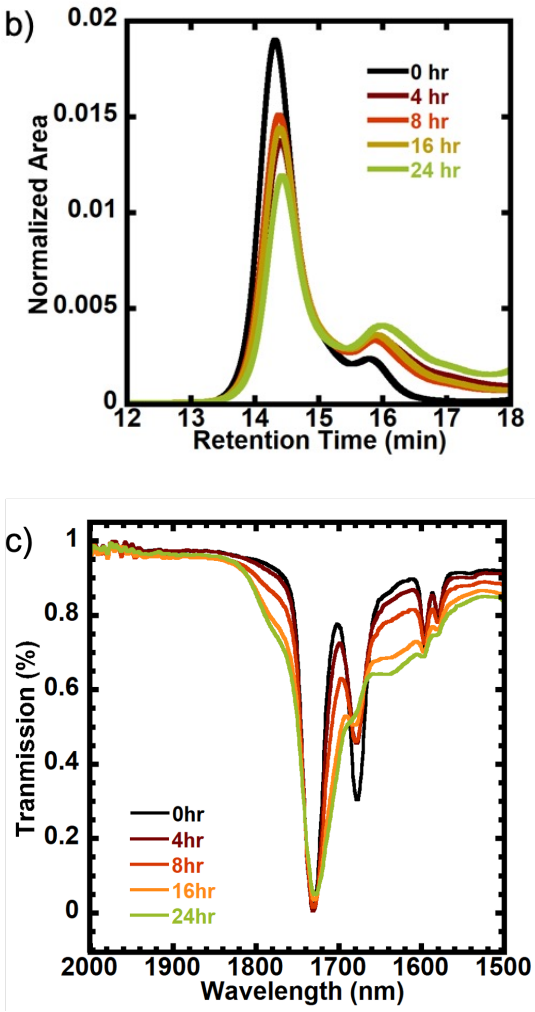



Figure 4: a). Tensile testing data for materials with $PVK_{150}$-$BA_{450}$-$PVK_{150}$ (40% PVK) with exposure to 310nm UV light over 0hr, 4hr, 8hr, 16hr, 24hr. b). SEC Analysis for the $PVK_{150}$-$BA_{450}$-$PVK_{150}$ (40% PVK) samples with exposure to 310nm UV light over 0hr, 4hr, 8hr, 16hr, 24hr. c). Expanded (wavelength region from 2000-1500 $cm^{-1}$) IR spectra overlap for $PVK_{150}$-$BA_{450}$-$PVK_{150}$ (40% PVK) material with exposure to 310nm UV light over 0hr, 4hr, 8hr, 16hr, 24hr

**UV induced Degradation**

Poly(vinyl ketones) are known for their degradability under UV radiation.[21,51] In our previous study on poly(PVK) materials, we observed efficient photodegradation of poly(PVK) homopolymers under 310 nm UV radiation and slow photodegradation under 350 nm UV radiation.[22] To observe the impact of the photodegradation of PVK on TPE materials, samples were irradiated with 310 nm UV radiation and the changes in their mechanical properties were

observed through tensile testing. In theory, cleavages in hard block segments would impact the strength of the hard domain which directly correlates with the toughness of the TPE materials. As predicted, our materials displayed loss of mechanical integrity, determined through tensile testing, upon irradiation with 310 nm UV radiation (Figure 4a). Similarly, SEC analysis displayed the formation of smaller molecular weight chains as a result of the cleaving longer tri-block polymers (Figure 4b). The main SEC peak only shifts slightly, as it is primarily the poly(BA) segments which do not degrade under 310 nm irradiation. However, during the UV degradation process, there was an increase in the low molecular weight polymer segments, which could correspond to the short poly(PVK) segments generated by the photodegradation. Both the PVK and BA molecules contain C=O moieties in their structures as ketones and esters respectively. The corresponding C=O stretches for PVK and BA appears in two different regions in IR spectra. IR analysis determined that the C=O stretching peak at 1660 $cm^{-1}$ corresponding to the keto groups in PVK degrade upon irradiation time, while the C=O stretching peak at 1740 $cm^{-1}$ for BA segments remains unchanged (Figure 4c). This data suggests that the chain cleavages only occur in the PVK blocks and not in the BA blocks. The literature proposes that the poly(PVK) degradation occurs through the Norrish type II mechanism.[22,52,53,54] The mechanical properties of the TPE materials were affected through this degradation process as shown in figure 4a, with their tensile strength reduced with increasing irradiation time. The degradation studies of these TPE materials were conducted under conditions, 49 $mW/cm^2$ UV radiation intensity, which would lead to much faster degradation than normal daylight. The UV region in sunlight covers a range from 100 nm- 400 nm which is further categorized as UVC (200- 280 nm), UVB (280-320 nm) and UVA (321-400 nm).[55] As the electromagnetic radiations pass through the atmosphere, almost all the UVC and most of UVB get absorbed by the ozone layer and the atmospheric gases.[56] UVC and

UVB have the most influence on the degradation of PVK than UVA radiation.[23] According to the previous studies, the peak intensity of UVB was less than 0.15 mW/cm$^2$ in most tropical and non-tropical countries.[57,58] Taking these facts into considerations, it can be estimated that our UV studies (under 49 mW/cm$^2$ light intensity) provide significantly faster (approximately 500 times faster) degradation for these TPE materials. Under ambient sunlight, these materials could last for 1-2 years until the PVK fully degrades.

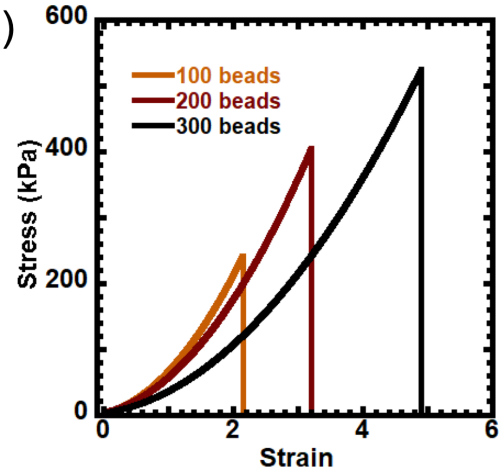
**MD Simulations**

To provide atomistic insights into the experiments, molecular dynamic (MD) simulations were performed with a coarse-grained model in which we used two different beads to represent hard (A) and softs (B) blocks in each chain. Initially, the polymer chains were designed and placed in a simulation box with no overlap with each-other. The initial configurations were then randomized and compressed within the simulation box until the desired volume obtained to generate the stress-strain curves (Figure S16). The interactions between each bead were calculated using Mie cut version of Lennard-Jones (LJ) potential.[59] The covalently bonded particles were represented with strong bonded interactions while the physical interactions between particles represented through weak non-bonded interactions (Figure S17).[60] Among non-bonded interactions (A-A, B-B and A-B), A-A$_{(non\text{-}bonded)}$ interactions were set to be the strongest while B-B$_{(non\text{-}bonded)}$ interactions set to be weaker in order to display the softness of the B matrix. Each non-bonded interaction values represent the affinity of the particles to others in the polymer matrix. Owing to the higher interaction values between hard block beads, they form clusters in the weakly interacting soft block matrix, mimicking the phase separation of typical thermoplastic elastomeric materials (Figure S18). The simulation domains were then stretched along the elongation axis (Figure S19) to generate the stress and strain curves using the overall atomic stresses and

elongation of the box respectively. A comparison between simulated system and experimental data was carried out with three different chain lengths (different number of beads) and five different blocks (beads) ratios (Table S4). We observed consistent trends in stress-strain curves between simulated and experimental systems (Figure 5a,b). Similar to the experimental parameters, when increasing the hard block portion, beads proportionally contain higher interactions. Hence, the moduli increase with the increment of the hard block segment.

In degradation, random chain scissions take place in the hard block segments. To mimic the degradation, we altered the bonded interactions between "A" beads at random points in the initial coordinates. In this alteration, at a set point in the chain (between beads $A_n$ and $A_{(n+1)}$), the bonded interaction set to be "zero". The set points were determined according to the percentage of the degradation (i.e. For 100 units long chain with 40% blue beads alterations were set at n=5 and n=97 to cleave 5 beads off from the 1$^{st}$ block and 3 beads off from the 2$^{nd}$ hard block to get 20% degradation). Graphically this displays as no bonds between "A" beads at the altered points (Figure S20). The initial randomized chains were then compressed to obtain the simulation domain with desired volume. Stress and strain curves were generated upon stretching the simulation domain. The tensile strength of the simulated systems declined with the proportion of random scission in hard block segments (Figure 5c). This mechanical loss upon scission of the hard block segments in the simulated system can be correlated with the experimental loss of mechanical integrity observed in materials with increasing UV irradiation time.

a)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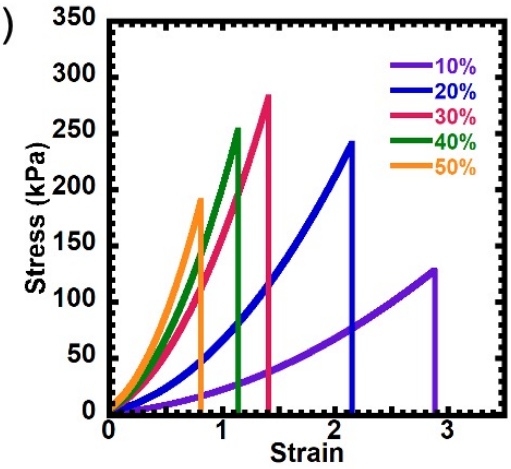
b)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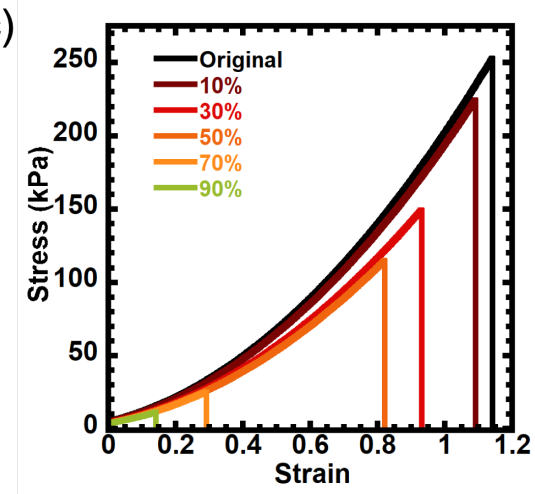
c)


Original
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1
1.2

Figure 5: MD simulation results for tensile testing data for a). bead systems with different length (20% A beads in each system): $A_{10}B_{80}A_{10}$ (100 beads), $A_{20}B_{160}A_{20}$ (200 beads), and $A_{30}B_{240}A_{30}$ (300 beads) b). 100 units long bead systems ($A_nB_xA_n$) with different A% s: $A_5B_{90}A_5$ (10%), $A_{10}B_{80}A_{10}$ (20%), $A_{15}B_{70}A_{15}$ (30%), $A_{20}B_{60}A_{20}$ (40%), $A_{25}B_{50}A_{25}$ (50%), c). Simulated degradation results for the 100 beads system ($A_{20}B_{60}A_{20}$) with 40% hard segment (Percentage of degradations were calculated by the ratio between number of disconnected "hard block" atoms from the original system vs total number of hard block in the original simulated system

**Conclusion:**

A series of poly(PVK-BA-PVK) triblock polymers were synthesized using RAFT polymerization under mild blue light with different chain lengths and PVK/BA ratios. The phase separation in these polymers systems was characterized through the presence of distinct transition temperatures and SAXS features. The mechanical properties of these materials were evaluated through tensile testing. An enhanced modulus was observed in tensile testing with increasing PVK hard block segments. Temperature sweep experiments showed the ability of these materials to hold their structure together even at higher temperatures with the presence of physical interactions. The TPEs can be reprocessed to obtain new materials with similar mechanical properties to the pristine samples. Upon irradiation with 310 nm UV light, the TPE materials lose their mechanical properties, due to the formation of low molecular weight poly(PVK) chains as a result of chain cleavages in PVK block. The photodegradation studies of these TPE materials under UV radiation provide insights about the ultimate fate of poly(PVK-BA-PVK) block polymers under sunlight.

Associated Content

**Supporting Information**. Experimental details, polymer molecular and spectroscopic characterization data, SEC peak deconvolution data, SAXS data, additional materials thermal characterization data, mechanical characterization data, and simulation details and snapshots are available.

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**Conflicts of Interest**

The authors declare no conflicts

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