

Segment Self-Orientational Behavior in Shape Memory Polymer Thin Films Probed by Raman Spectroscopy

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ABSTRACT: Understanding the relationship between the phase separation and domain orientation of segmented block copolymer within thin-film samples is crucial for a complete picture of their physical properties, and hence for the worldwide development of smart materials, and in particular, shape memory textile technology (Hu et al.^{1–3}). We report here on the efficacy of polarized Raman spectroscopy (RS) as a probe of phase separation and average molecular orientation, presenting results for segmented block copolymer thin films with various hard segment contents. A comparison is made with the results of differential scanning calorimetry (DSC). We show in many cases phase separation and domain orientation can be more directly characterized by polarized RS, and that it offers more information on the

degree of molecular orientation than conventional thermal measurements. Raman scattering of phase separation in block copolymers has not yet been exploited to provide complementary microscopic information where other techniques are not applicable. The fact that Raman spectrum can be collected *in situ*, with diffraction limited resolution and chemical specificity makes the technique widely applicable as a noninvasive probe. This study provides clear evidence on the unique molecular ordering in segmented blocked copolymers used in shape memory thin films. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 765–770, 2007

Key words: shape-memory; polyurethane; Raman; soft segment; hard segment; crystallization

INTRODUCTION

Shape memory polymers are thermoplastic segmented block copolymers having a wide range of glass transition temperatures. They are the synthesis of $[(H)_x(S)]_n$ -type statistical copolymers, in which there are x and n repeat units of hard and soft segments in each polymer chain, respectively. Foremost among the unique mechanical properties of this class of copolymers are the pseudoelasticity and thermal-responsive shape memory effect. That is, the material can restore its original shape upon heating above certain temperature after being strained. This unique feature has made this type of material arouse serious research interests from both academia and industry in recent two decades.^{1–9} The contemporary picture on the film morphology itself can be rationalized by taking into account the thermodynamically incompatibility between the rubbery soft segment (SS) and hard segment (HS) sequences, forming the so-called micro-phase-separated heterogeneous structure scenario.¹⁰ The shape memory effect, in particular, utilizes the amorphous SS domains as the revers-

ible phase, and crystalline HS domains as frozen phase.¹¹ The HS domains act as a thermally labile physical crosslink sites and fillers for the rubbery phase, rendering long range elasticity soft micro-domain matrix.^{12,13} The shape memory effect is greatly depended upon the SS and HS molecular weight and their relative contents within the films.^{11,14} This in turn affects the film morphology resulting from the interplay between the two incompatible components. Good shape memory effects have been observed with transpolyisoprene (TP1),¹⁵ styrene-butadiene copolymer (SB),¹⁶ and segmented polyurethanes (PUs).¹⁷ In terms of the biostability performance, the merit of using biomedical PUs again has taken the interconnecting hard micro-domain texture into account.¹⁸

Knowing in advance the important role of HS in segmented copolymers, or its influence on the overall film characteristics, there have been many attempts to probe the morphological features of segmented copolymers as well as their mechanical integrity during/after deformation process. The solid state surface morphology of segmented PUs can be examined by small-angle X-ray scattering (SAXS),^{19,20} and thermal analysis,^{21,22} as well as transmission electron microscopy (TEM).^{23,24} Until recently, tapping mode atomic force microscopy (AFM) has been employed to elucidate the micro-domain formation structure with nanoscale resolution.^{25,26} The structural change and chain orien-

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tational behavior of segmented PUs during tensile deformation can be characterized by dynamic mechanical thermal analysis (DMTA), wide-angle X-ray diffraction (WAXD), stress hysteresis, and infrared dichroism.^{27–29} SAXS provides many quantitative data about the specimens, such as on the interdomain spacings, degree of phase separation, interfacial thickness characteristic, etc. However, real-space visual characterization of the dispersion of microdomains and their evolution are not feasible using this technique. The use of TEM provides a high magnification real-space morphological image, but the technique depends on the efficacy of the staining method, and is limited by the possibility of beam damage on samples such as polymers. The use of AFM to investigate film morphology is now well established. However, this technique requires time-consuming prior sample surface preparation procedures such as cutting of microtome slices as in the case of TEM. On the basis of the mentioned technique, there is neither conclusive evidence emphasis on the hard/soft segmental conformation as a whole nor focuses on the molecular orientation within segments in particular. Most of the researches on observing the formation of micro-phase separation in many cases offer only an ensemble picture of the overall segmental behavior.

In this study, polarized Raman technique is used to further elucidate the micro-domain formation and degree of molecular orientation in the HS domains, respectively, within films of segmented PUs. To probe the local molecular alignment and phase separation within thin film samples with different HS concentrations, the polarization selection rules of a specific Raman active mode in the HS domains are employed. The crossovers between the three different physical morphologies in these copolymers were identified and compared with that from DSC thermal analysis, accordingly. The Raman data provides an evidence of showing the unique molecular orientation of the interconnecting crystalline phase at high HS content. We believe these procedures not only provide and *in situ* characterization with emphasis on the phase separation–orientation relationship but also offer a sensitive structure probe used in the fabrication and processing of segmented copolymers used in shape memory textile technology.

EXPERIMENTAL

Segmented block PUs containing different HS contents were synthesized with polycaprolactone diol (PCL) having molecular weight 4000 (hereafter, PCL4000) as the SSs and with 4,4'-diphenylmethane diisocyanate (MDI) chain extended with 1,4-butanediol (BD) as the HSs. All the chemicals used in the study

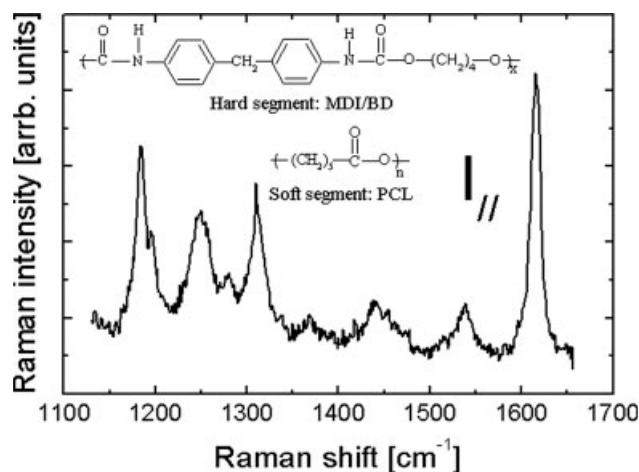


Figure 1 Polarized Raman spectrum obtained from a PU film, with 633 nm-laser as the excitation source. Inset shows the schematic of both the hard and SSs made up the copolymer.

were of analytical grade. The series of PU samples is designated as PU-XX, where XX denotes the weight percentage of the HS.

Both the PCL4000 from Daicel and the solvent *N,N'*-dimethylformamide (DMF) from Aldrich were dried at 80°C in vacuum for 6 h and with 4 Å-molecular sieves prior to measurements, respectively. The PUs were prepared by a two-step polymerization with 5% excess MDI content to ensure complete reaction. The NCO-terminated prepolymers were first prepared by reacting the dried PCL4000 with the mole excessive MDI (Acros) in the DMF solution at 65°C for 3 h. The prepolymers were chain extended with BD (International Laboratory USA) at 80°C for another 4 h, subsequently. Schematic chemical structures for the hard and SSs are shown in the inset of Figure 1. The PU films with different HS contents were transferred to a Teflon mold and allowed it to solidify at 80°C in air for 24 h. To remove the residual DMF, the films were held at the same temperature in vacuum for 24 h subsequently. The nominal thickness of the films was about 50 μm measured by a Dektak profilometer.

Raman spectra were recorded over the range 1150–1650 cm⁻¹ with a Renishaw 2000 spectrometer coupled to an Olympus BH-2 microscope. A long working distance objective of magnification X20 was used to focus the 633 nm excitation laser with a power of about ~ 2 mW on the PU films. Integration times for each polarized spectrum was 20 s with up to three scans accumulation. Following a curve-fitting routine (Grams 32, Galactic Industries, Salem) at the ~ 1616 cm⁻¹ vibrational mode, the magnitude of the peaks are plotted with various HS contents.

The thermal properties of the segmented PUs were investigated by the Perkin-Elmer Diamond

DSC, purged with nitrogen gas and cooled by an intracooler. To ensure a consistent thermal history for the melting process, all the specimens were heated twice at a heating rate of 10°C/min from -50 to 250°C and the second thermograms were recorded and compared.

RESULTS AND DISCUSSION

Raman depolarization in solids

In this section, we show that Raman scattering offers the possibility of *in situ* monitoring of segmental phase separation. The shortcoming of this specific application is the difficulty to correlate the data with the detailed structure change. The phase separation and structure of the block copolymer studied here have been investigated by many techniques based on X-rays and thermal analyses as mentioned before, but the quantitative linkage between the Raman data to that from other techniques is still missing due to the fact that the cause of the structural changes and its effect on the scattering data is not direct. Nevertheless, it is worth to demonstrate a straight forward optical technique to monitor the phase separation. In addition, it is important if the technique is noninvasive and able to monitor the film quality in terms of phase separation and molecular orientation during the fabrication process.

We first turn to the specific Raman spectrum in our measurement. Figure 1 shows the polarized backscattered Raman intensity, $I_{//}$, from a PU film with 50% HS content at room temperature. We used a microscope objective having small numerical aperture (NA = 0.2) to provide an axial resolution of about $\sim 50 \mu\text{m}$. ($\Delta_{\text{axial}} = 2\lambda n / (\text{NA})^2$, assuming $n \sim 1.5$, and $\lambda = 633 \text{ nm}$). This ensures that only scattering signals coming from a film layer of $\sim 50 \mu\text{m}$ centered on the focal plane are scattered and collected by the spectrometer. This length is about the average thickness of all the PU films used in this study. The lateral resolution is much better $\sim 2 \mu\text{m}$ ($\Delta_{\text{lat}} = 0.61\lambda / \text{NA}$). We only pay attention to the highest peak at $\sim 1616 \text{ cm}^{-1}$ in the Raman spectrum. This vibrational mode is indeed not greatly perturbed by the detailed chemical structure in the main PU chain, resulting in a benzene-like vibrational mode with similarity in both frequency and symmetry. The nonresonance Raman intensity I for a specific vibrational mode is given by^{30,31} $I \propto |e_s^p \cdot \hat{R} \cdot e_L^p|^2$, where \hat{R} denotes the Raman tensor determining the selection rules for nonresonant RS in liquids and crystals, e_L^p and e_s^p are the unit vectors of the excitation and scattered radiation polarization directions. The depolarization ratio of a vibrational mode, to wit: $\rho = I_{\perp} / I_{//}$, where I_{\perp} and $I_{//}$ are the average perpendicular and parallel intensities over all possible orientations with polarizations relative to that of the excitation

laser, respectively, is a normalized intensity ratio which can be used to provide some information on the tensor components of \hat{R} .^{32,33} It contains information on the average molecular orientation because it normalizes any local variations in scattering volume. It is worth mentioning that the maximum value of ρ (with uni- or bi-axial point groups having totally symmetric (Γ_1) vibrations) is 3/4, which occurs when \hat{R} is traceless for a collection of randomly oriented molecules.³⁴ The situations involving strong uniaxial character may fix the ρ value to either 1/3 or 1/8. These special cases require \hat{R} has either one or two vanishing diagonal elements.

It is worth noting that a value of $\rho \sim 1$ indicates the benzene rings in the PU backbone lie to a large extent parallel to the film surface. We have never obtained any ρ with a unity value in our PU films in any cases. This special value can be obtained from a different class of material, namely conjugated polymers, which have been used extensively in light emitting diodes (LEDs), thin film transistors, and solar cells.^{32,33,35} In fact, $\rho \sim 1/3$ suggests that the rings rearrange themselves perpendicular to the film surface. On the other hand, $\rho \sim 3/4$ suggests a random orientation of the benzene rings on average.

Relationship between molecular orientation and phase separation

We have performed the polarized Raman measurements on the PU films with different HS contents. The polarized Raman intensities denoted by $I_{//}$ and I_{\perp} at $\sim 1616 \text{ cm}^{-1}$ mode are displayed in Figure 2(a). Both the intensities rise in a step way to reach maximum values with increasing HS contents. In general, $I_{//}$ and I_{\perp} are proportional to the local thickness of the PU film through the scattering volume and contain the information on the symmetry of the mode. The low axial resolution of the Raman probe and large film thickness, both are $\sim 50 \mu\text{m}$, has diminished the effect of local thickness variation, which is believed to be smaller than $1 \mu\text{m}$. This can also be realized by the gradually change of both the intensities with less scattered data. An average value of $\rho \sim 0.71$ on the left part of Figure 2(b) suggests that the benzene rings are initially oriented randomly in the films at low HS content. The ρ values are not dependent on the rotation of the PU films for a fixed set of polarizations. The intuitive picture is that the HSs of which the film is partly composed arrange themselves randomly at low HS contents (<25% in our case). The challenge here is to understand the departures of the ρ from the original value—a signature that molecular ordering is quenched during the cooling process in forming the film. As the HS content is above a particular value $\sim 25\%$ as shown in Figure 2(a), there is an abrupt

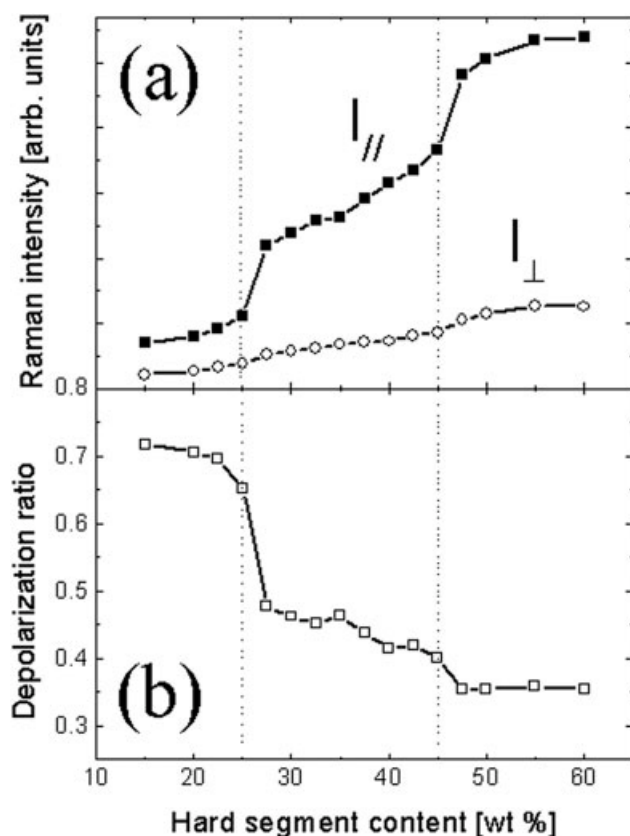


Figure 2 (a) Polarized Raman intensities of the PU films with various HS contents. $I_{//}$ and I_{\perp} denote the signals with polarization parallel and perpendicular to that of the excitation laser, respectively. (b) The plot of peak intensity at $\sim 1616 \text{ cm}^{-1}$ vibrational mode with various HS contents. There exists two critical HS weight percentages, ~ 25 and 45% , respectively, which divide the molecular orientation into three categories. The first one is the randomly oriented HS, the second is the less random HS conformation, and the last the nearly perpendicular aligned HS.

increase in the polarized signals, which is more pronounced for the parallel polarization. It is suggested that a new phase of HS is decoupled from the soft-matrix as a result of the high incompatibility between the hard and Ss.¹⁴ The depolarization ratio is ~ 0.45 with the HS content lies between 25 and 45%, indicating that the HS domains orient themselves in a certain configuration apart from a random fashion. Within this HS range, the ρ values are not totally independent of the HS content. The exact molecular conformation can be further elucidated by interpreting the ρ values when the HS content is higher than 45%. A value of $\rho \sim 0.35$ suggests that the benzene rings are now to a large extent perpendicular to the film surface at this high HS content. The evolution of the ρ values from ~ 0.71 to ~ 0.35 concludes the existence of a transition region in which the benzene rings in the HS start to demix from the matrix and orient themselves to lie perpendicularly to the film surface. The experimental result is in agreement with the observation by Martin et al.

to some extent.³⁶ The authors observed an increase in HS content above 45% resulted in interconnection between hard micro-domains, forming a continuous morphology. The question of whether the crystallizable hard micro-domains exhibit discrete morphology when the content is below 45% in the PU films is difficult to identify by the Raman probe at this stage. Notwithstanding this, the average molecular orientations can still be quantified by this technique with intermediate HS content. The depolarization ratio of the PU film suggests that the in-plane vibrations of the two benzene rings contribute a high uniaxial Raman tensor. The most appropriate Raman tensor for this vibrational mode is

$$\hat{R} = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (1)$$

where $a, b \ll 1$. This tensor is similar to that for the 1605 cm^{-1} phenylene vibrational mode in highly uniaxial aligned polyfluorene films³⁵ and is in agreement with the in-plane stretching mode for the mono- or di-substituted benzene (Γ_2 representation of C_{2v}). Partial ordering of molecules in their liquid state where isotropic averaging of the Raman tensor is partially broken down is crucial for the strong anisotropic property in liquid crystals. The high uniaxial character of the tensor components coincides with the main geometrical axis of the molecule, providing a direct probe of the physical molecular alignment. The $\alpha_{zz} = 1$ diagonal element is parallel (but perpendicular to the film surface) to the two benzene rings in the backbone of the PU. The implication of the HS orientation and micro-domain morphology on the tensile properties is profound. It is well known that the domains respond differently depending on their initial distribution. This in turn determines the deformation modes of the film, i.e., either lamellar separation or shear compression or both. The orientation function (obtained from infrared dichroism measurement) of the HS decreases at low draw ratios which is related to the rotation of the long axis of HS. However, the situation will be different when the HS content is above the threshold value $\sim 25\%$, especially when the interdomain interaction exists. To obtain a complete picture of the plastic deformation of the HS domains at high HS content $>25\%$, the molecular orientation within the HS domains, its response to the drawing direction, and its impact on the axial and lateral strengths of the film should all be taken into account. This in turn provides a direct impact on the fundamental physics of the mechanism in describing the shape memory effect. By using the same experimental technique, the structure changes and chain orientational behavior during tensile deformation is now being studied. The

underlying idea is to monitor the different chemical dynamics, such as the free- and hydrogen-bonded C=O which can be used as the identification tags representing the deformation behavior of the chains in soft and HSs, respectively, upon drawing the PU films. The data collection for this measurement is underway and will be reported elsewhere.

The problem of phase separation in segmented block copolymers with various soft/hard contents deserves further investigation. In general, copolymers have the unique ability to self-assemble into various oriented structures. Above a critical monomer concentration, the weak repulsion between two unlike monomers S and H cause another to segregate. The immiscibility of these monomers drives the whole system to form a particular structure so as to minimize the contacts between them. This is the driving force of the tendency for the two monomers separating into H- and S-rich domains, but at the same time this force is counter balanced by the entropy cost associated with stretching the polymer chains. This energetic competition results in the phase separation on a mesoscopic scale with H- or S-rich micro-domains. These mesoscopic domains can be, highly regular, such as lamellar, circular tubes, etc.^{37,38} However, the Raman tensor in (1) describes the hard micro-domains as having a special form of lamellar structure. The distribution of the long axis of the hard micro-domains can be randomly oriented within the 2 dimensional-plane of the film, but the benzene rings of which the HS is composed lie perpendicularly to the film surface. The benzene rings themselves lie parallel to each other provided that they are forming the lamellar structure. A manifestation of interfacial preordering effect can be induced by the local stretching of polymer chains and the locally one-dimensional structure drive the retention of layer planes on crystallization from an ordered melt.³⁹ As a result, a complex soft structure can direct the crystallization processes, selecting a specific orientations. The selection process is dictated by the subtlety in the local chain orientation. This ordered structure is the key to the material properties which makes segmented block copolymers of great technological importance. This molecular order is entropic in nature regardless of the presence of liquid crystalline phase and volume interactions. In general, any measurable physical properties or parameters depending on the detailed molecular averaging within the film will be altered, accordingly. In particular, the Raman intensities and depolarization ratio in our case are perturbed. To mathematically model this phenomenon, three dimensionless parameters are needed for the micro-domain formation: the Flory–Huggins interaction parameter to measure the incompatibility of the two components, and the degree of polymerization of the

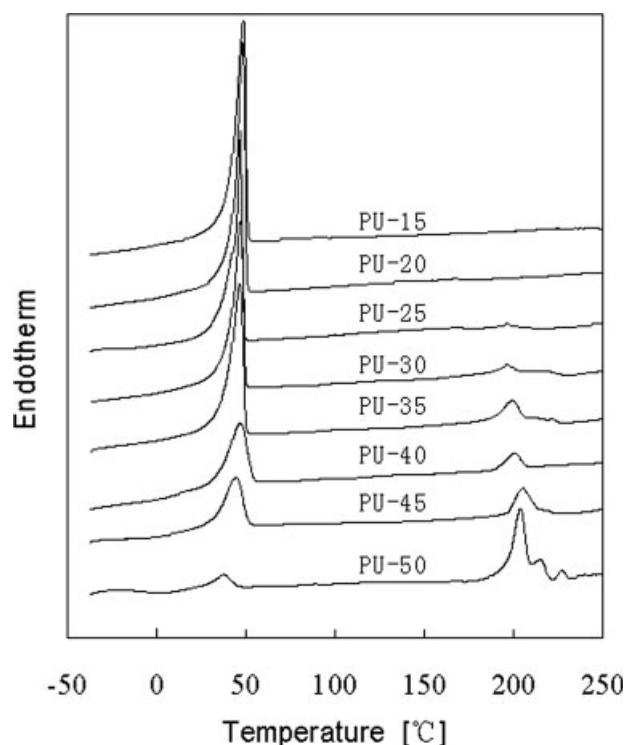


Figure 3 DSC thermograms of the PU with varying HS contents. The series of PU samples is designed as PU-XX, where XX denotes the weight percentage of the HS.

two polymers, as well as the relative length scale between the two monomers. Unfortunately, these constants are not known for our copolymers. Nonetheless, the Raman data in this study, do suggest that phase separation exists in the PU films, and the change in the depolarization values (i) locate the crossover concentrations of the HS, and (ii) suggest the average molecular orientation within the hard micro-domains for different HS contents. We conclude in this paragraph that Raman spectroscopy (RS) in thin segmented block copolymer films can render information on the phase separation and hard segmental molecular orientation at different HS contents.

Comparison between Raman and DSC data

DSC measurements were performed on the same batch of PCL4000 films to provide a direct comparison of the threshold HS values. As shown in Figure 3, the DSC thermograms reveal significant endothermic features in the temperature scan. The higher temperature peaks feature a gradual increase in the enthalpy of fusion (above 25% HS) responsible for the HS phase transformation at the expense of that for the SS. An increase in HS content results in an increase in hard micro-domain crystallinity. The multi-endothermic behavior shown in the figure at high HS content has been well studied by Koberstein et al.²² The authors used simultaneous SAXS

technique to show that the high temperature endotherm at high HS content can be ascribed to the melting and immediate melt recrystallization of the HS crystals. The melting enthalpy of the SS decreases with increasing HS content. It is observed from Figure 3 that the HS content in the films affects the melting behavior of the SS. The melting temperatures of the SS are reduced a few degrees with increasing HS content in analogous to the so called depression of melting point phenomenon. The shift of the melting temperatures is a clear consequence of the concentration dependent miscibility between the hard and SSs. The DSC thermograms on the HS reveal (i) there exists a lower threshold HS content $\sim 25\%$ where the enthalpy of fusion starts, representing by a weak feature in the temperature scan, and (ii), a higher threshold HS content $\sim 45\%$ above which the curve show multi-endothermic characteristic. The DSC temperature scans provide consistent HS threshold values as in the case of RS.

CONCLUSIONS

Segmental orientation behavior was probed with polarized RS. The orientation of the crystalline HS was obtained from the in-plane vibrational mode of the two benzene rings at $\sim 1616\text{ cm}^{-1}$. The Raman data provides evidence for the segmental orientation transition from a randomly to partially aligned hard micro-domain internal structure when the HS content is above a critical value $\sim 25\%$ in the PU film. However, these partially aligned micro-domains can reach totally aligned configuration as the HS content is above 45%. It was found that the benzene units of which the HS is composed preferentially orient themselves perpendicularly to the film surface. The measured concentration dependences of the micro-domain alignment provides a consistent interpretation of our data with that by using SAXS and DSC,^{22,40} and thus validate the Raman technique used in this study. Lastly, we have performed the DSC scan to further demonstrate the efficacy of RS in this application by comparing the onset HS contents for the crossover between different phases in PU film.

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