ACS Macro Letters

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Letter

Dynamic Mechanical Analysis of Polymer Thin Films Using a Kirigami-Inspired Support

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Cite This: *ACS Macro Lett.* 2021, 10, 1107−1112

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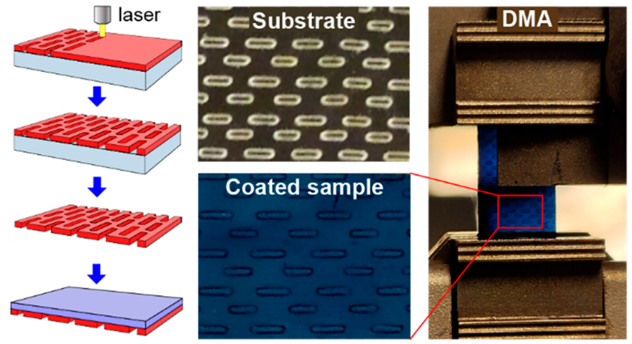
ABSTRACT: A method of determining the mechanical relaxation behavior of polymer thin films is presented that employs a kirigami-inspired sample support. The film of interest is placed on the kirigami support and loaded into a dynamic mechanical analyzer. When the composite is placed in tension, the substrate effectively transfers the load to the film of interest. We demonstrate the approach using a number of polymers and conjugated polymer: small molecule blends relevant for organic photovoltaics. The kirigami-inspired method is found to provide an accurate view of thermal relaxation behavior in polymer thin films, including a quantitative assessment of the film storage modulus. The method is particularly valuable in thin films where film morphology is highly dependent on processing conditions. We show that differences in casting conditions have a clear impact on the thermal relaxation of both the neat and blend conjugated polymer films.



A clear view of the thermal relaxation behavior of polymer thin films is important for a range of applications from protective coatings to thin film electronics.[1−3] This is particularly true for flexible and stretchable organic electronics that are required to be mechanically robust. The viscoelastic behavior of conjugated polymers has been found to provide insight into the mechanical reliability of devices.[4,5] For example, a recent study by Balar et al. has shown that the secondary thermal relaxations observed in conjugated polymers play an important role in film toughness.[6] In addition, thermomechanical behavior has been connected to morphological stability, particularly in blend films that are cast out of thermal equilibrium, as is typically the case for bulk heterojunction (BHJ) organic photovoltaics (OPVs).[7−9] This is exemplified by considering the highly efficient PM6:Y6 based solar cell that shows a 10% reduction in power conversion efficiency after 30 days of aging in a N_2 environment due in part to morphological instability.[9] Thus, an accurate view of the thermal behavior is needed to guide the development of mechanically robust and physically stable organic electronics.

To detect conjugated polymer thermal relaxation behavior, several methods have been employed, including differential scanning calorimetry (DSC),[10] plasmonic nanospectroscopy,[11] ellipsometry,[12] shear rheometry,[13] UV−visible spectroscopy,[14] and dynamic mechanical analysis (DMA). DSC is the most widely used method; however, it often lacks the sensitivity to detect thermal relaxations in donor−acceptor (D-A)-type conjugated polymers.[9,15] Alternatively, DMA is known to be one of the most sensitive tools to measure thermal relaxations and has been shown to capture the relaxation behavior of D−A polymers well.[1,6] Given the high costs and limit laboratory scale quantities of conjugated polymers, it is difficult to create free-standing specimens for DMA tests. To overcome this limitation, there have been several alternative specimen configurations employed. Methods include the use of a powder clamp that uses flexural forces on the powder sample to assess relaxation behavior.[16] However, this approach still requires a relatively large amount of material for each run (>10 mg), and the results have a low signal-to-noise ratio. More recently, a polymer impregnated woven glass mesh based technique has been introduced;[1,2] wherein the polymer is drop cast onto a glass mesh and when loaded into the DMA, the load on the glass mesh is effectively transferred to the polymer of interest. This approach has been found to be an effective method to study the thermal relaxation behavior of conjugated polymers.[1,6] However, the drop-cast process hinders control over sample morphology, and the impregnation process limits the knowledge of film thickness under load. Without the knowledge of film thickness, the quantitative assessment of the storage and loss modulus is not possible. The lack of morphology control can also have significant implications

Received: June 12, 2021
Accepted: August 9, 2021

https://doi.org/10.1021/acsmacrolett.1c00396
ACS Macro Lett. 2021, 10, 1107−1112

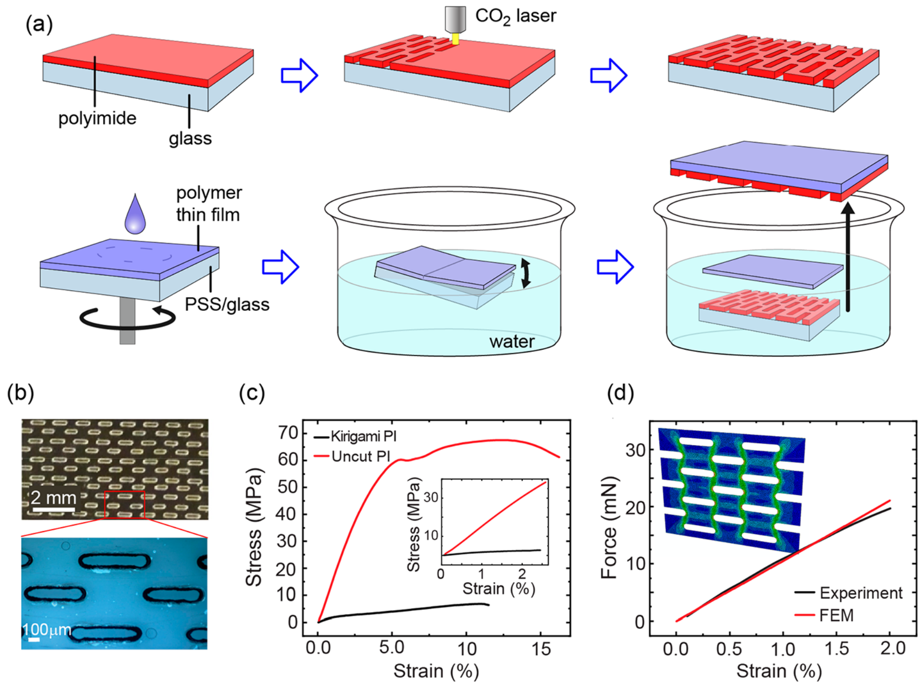


Figure 1. (a) Schematic of the processing steps to fabricate the KIT sample that include creating the kirigami cut in thin PI film using a laser cutter, floating the thin polymer film on water and picking it up using the KIT substrate to make the composite. (b) Image of the optimized kirigami cut pattern. (c) Uniaxial tensile tests of neat PI film and KIT support tested at a strain rate of 5%/min. (d) Comparison of the stress−strain response of the KIT support with finite element modeling with inset showing the modeled stress distribution.

when correlating thermomechanical behavior to device characteristics. For example, when considering a low miscibility blend, which is often found in BHJ OPVs, the drop cast approach may result in phase separation that would not correspond to device-relevant film morphology[7,17] and may impact thermomechanical properties. Lastly, Akabori et al. introduced a composite approach with the polymer film of interest coated on a 7.5 μm thick polyimide (PI) substrate.[18] The stiff and relatively thick PI substrate required that the film of interest be made very thick. To overcome the overshadowing effect of the stiff substrate, Lu et al. employed a much thinner PI substrate with a thickness of 600 nm.[4] In this case, the thermal relaxation of DPP-based conjugated polymers with a thickness down to approximately 250 nm could be measured.[4] While the thinner PI approach improves measurement sensitivity, it still lacked the sensitivity to detect subtle thermal relaxations often observed in conjugated polymers. The ultrathin nature of the substrate also makes handling the sample a challenge. Thus, there remains a need to develop DMA test methods that can provide precise and sensitive measurements of thin polymer films that are processed using approaches consistent with device fabrication and with a known film thickness for quantitative mechanical property assessment.

Here, we introduce a method of measuring the thermomechanical behavior of polymer thin films using DMA that combines aspects of the glass mesh and the thin polyimide support approaches, which we refer to as the kirigami-inspired thin-film (KIT) test method. The method, illustrated in Figure 1, uses a thin polyimide substrate with cuts distributed across it. The substrate provides support for the thin film of interest. When the load is applied, the substrate cuts open up, effectively transferring the load from the substrate to the polymer film. The load transfer to the thin film allows for direct characterization of the film's thermomechanical behavior. By subtracting the force required to strain the patterned PI substrate, the storage modulus of the thin film can be determined over a broad temperature range. In this paper, we describe the sample preparation approach, the measurement method, and explore the capabilities of the approach. We use the method to probe the relaxation behavior in several polymer and polymer/small molecule acceptor semiconductor blends, including polystyrene (PS), P3HT, PTB7-TH, PM6, and IEICO-4F, with their molecular structures given in Figure S1. We compare the KIT test method to the impregnated glass-mesh approach, showing how differences in sample processing can lead to changes in the relaxation behavior of the sample highlighting the strengths of the technique. Specifically, using the KIT method, we are able to capture changes in thermal relaxation behavior of the conjugated polymers and BHJ films based on casting conditions and small molecule load fraction.

PI was selected as the substrate due to its toughness and thermal stability over a broad temperature range, with a glass transition temperature (T_g) over 260 °C and a weak secondary relaxation (sub-T_g) between approximately 137−150 °C.[19,20] We use a PI resin that can be solution processed into thin films and kirigami patterns were introduced into the films through CO_2 laser ablation (see Supporting Information for experimental details).[21] Incorporation of the cut pattern in the PI substrate dramatically reduces the stiffness of the substrate; however, if the cuts are too large or dense, the substrate becomes prone to failure. Thus, design optimization is needed to minimize the stiffness of the substrate while maintaining stability over a broad range of loading conditions (temperature, frequency, and strain). There is also a need for the cut pattern to be designed such that the thin film placed on the substrate does not mechanically fail during testing. We focus on a simple

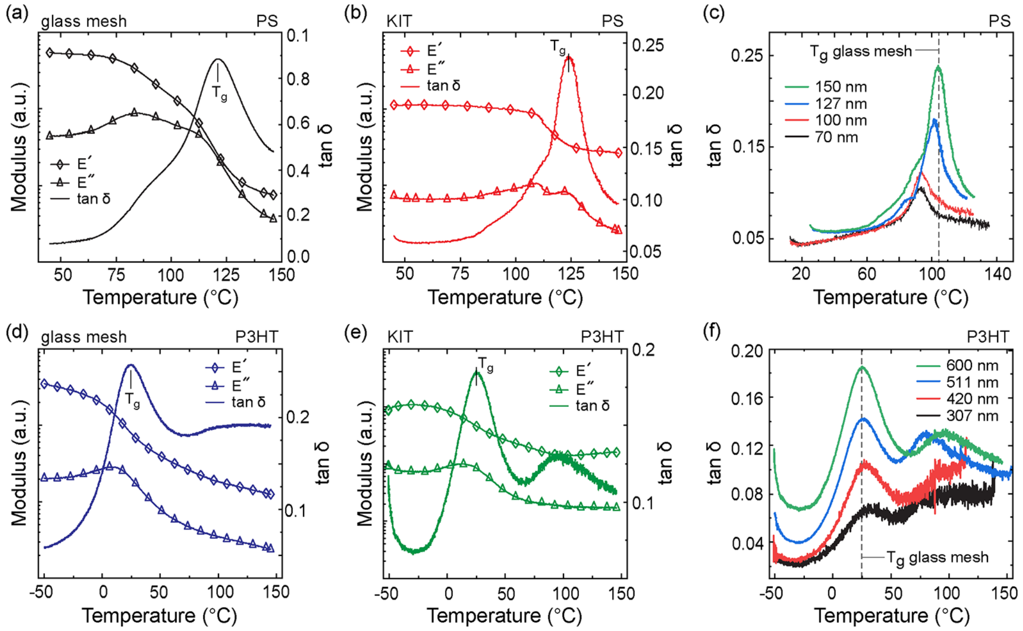


Figure 2. DMA scans of (a) PS on the glass mesh support, (b) PS on KIT support with a film thickness of 150 nm, and (c) loss tangent of PS as a function of film thickness. DMA scans of (d) P3HT on the glass mesh support, (e) P3HT on the KIT support with film thickness of 600 nm, and (f) loss tangent of P3HT as a function of film thickness.

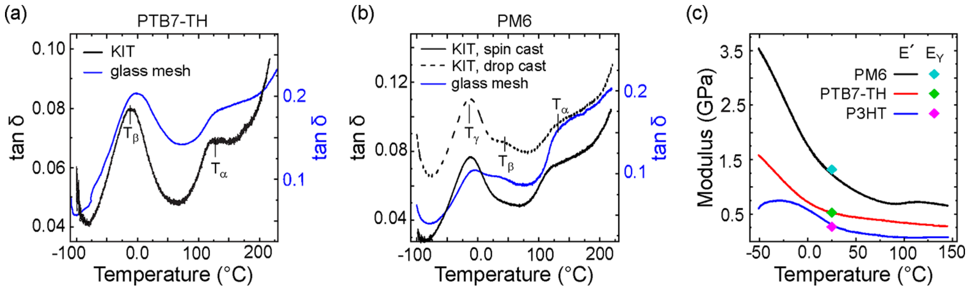


Figure 3. Comparison of the loss tangent of (a) PTB7-TH and (b) PM6 for samples on the glass mesh and KIT support. PTB7-TH and PM6 film thicknesses were 615 and 567 nm, respectively. (c) The storage modulus of PTB7-TH, PM6, and P3HT and comparison to the measured Young's modulus (E_Y) at room temperature.

parallel cut pattern, as shown in Figure 1. Other cut patterns were explored but were not found to be as effective with details provided in the Supporting Information (Figures S2 and S3). An image of the optimized cut pattern is shown in Figure 1b, which provided a good combination of compliance and physical stability. The stress−strain response of the optimized substrate was compared with the uncut PI substrate, with results given in Figure 1c. It was found that the effective Young's modulus (slope of the stress strain curve up to 1% strain) drops from 2 GPa for the uncut PI substrate to under 0.23 GPa for the patterned substrate highlighting the large drop in stiffness achieved. Finite element analysis (FEA) of the cut pattern is also provided in Figure 1d, showing well-matched behavior to the experimental results. The FEA provides a means to design cut patterns to minimize the stress concentrations in the PI support that may lead to sample failure. Here, we observe the local stress in the KIT substrate is kept minimal, particularly with the round edges of the cuts provided by the laser cutter. It is important to note that the specific cut pattern was varied for a given sample to ensure thin film stability during testing, including changes in cut width. It was found that the kirigami support with larger cut widths improved measurement sensitivity but led to fracture of brittle thin films. Thus, we varied the laser cutter power from 8−60% to achieve cut widths between 80 and 160 μm.

We start by considering the PS and P3HT thin films that represent a fairly large difference in Young's modulus (E_Y) at room temperature from approximately 0.26 GPa for P3HT to 2.5 GPa for PS.[6,22] In both cases, we compare the thermal relaxation behavior measured with the KIT approach to that measured using the impregnated glass mesh approach. The storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) of the polymers using both test methods is given in Figure 2. We find that the methods produce similar T_gs, defined here as the peak in tan δ. The measured T_gs are also consistent with previous reports.[1,6,16] The relaxation behavior of P3HT using the kirigami polyimide substrate was also compared to an uncut PI substrate, with results given in Figure S4(b). Without the cut pattern in the substrate, the T_g of the P3HT could not be observed. To explore the sensitivity limits of the KIT method, we measured the relaxation behavior of the P3HT and PS films as a function of thickness, with results given in Figures 2c,f and S5. The film thickness was varied by changing the casting conditions. In the case of thick P3HT samples, thick films were made by stacking multiple films. The T_g is clearly observed with film thickness as low as 307 nm for P3HT and

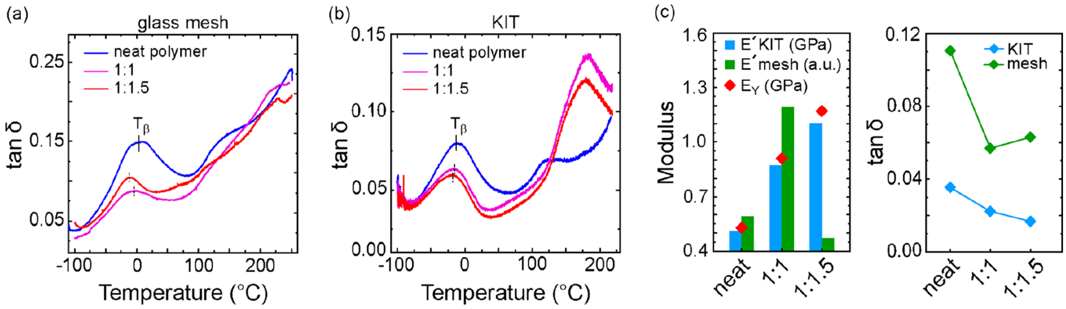


Figure 4. (a) Tan δ comparison of neat PTB7-TH and PTB7-TH:IEICO-4F blend films using (a) the glass-mesh support and (b) the kirigami support. (c) The change in storage modulus and tan δ at T_β (marked in a and b) of the neat and blend films using the glass-mesh and KIT supports. The storage modulus is also compared to Young's modulus (E_Y), measured with FOW tests. The glass-mesh modulus is given in arbitrary units given the unknown film thickness.

70 nm for PS films. The stiffer PS made it possible to measure thinner films compared to P3HT. We limited PS to 70 nm thick films as handling became more difficult for thinner films. It should be possible to go to even thinner films with processing and substrate optimization. In the P3HT samples, the measured T_g is constant with film thickness. In the PS samples, we observe a drop in T_g for the 100 and 70 nm thick films. This may be associated with the thin film confinement effect or differences in film morphology.[23,24] The confinement effect and T_g suppression have previously been shown to depend on the film being free-standing or supported.[25] In the KIT method, there is a combination of free-standing and supported film that we believe both contribute to the observed behavior. Future research will explore the respective contributions and their role in the observed change in T_g.

In addition to P3HT and PS, the thermal relaxation behavior of the polymers PTB7-TH and PM6 was measured with tan δ given in Figure 3 and E' and E'' given in Figures S6 and S9. These materials are chosen, as they represent high performance D−A conjugated polymers that show thermal relaxations that do not conform to a classic glass transition.[1,6] When comparing the glass mesh approach and the KIT method, the thermal relaxation behavior largely follows a similar trend for both polymers, as shown in Figure 3. However, the PM6 glass-mesh sample shows a thermal relaxation feature at approximately 40 °C that is not observed in the spun-cast polymer on the KIT support. To determine the origin of this behavior, we tested a drop-cast PM6 film on the KIT support. As shown in Figure 4b, the drop-cast KIT specimens also show the relaxation at 40 °C, similar to the glass mesh specimens. These results highlight potential morphological influences and the need to characterize the thermomechanical behavior of device-relevant films.

An important feature of the data is that the tan δ using the KIT method is lower than that found for the glass-mesh approach, which in turn is lower than that typically found in bulk sample tests. This drop in tan δ with sample support is likely associated with the lower viscous dissipation behavior of the substrate and the potential interfacial damping.[26,27] The lower tan δ for the KIT method as compared to the glass mesh samples is likely due to the stiffer substrate of the PI substrate compared to the glass fiber mesh and the reduced amount of sample materials in the KIT specimen. As observed in Figure 2c,f, as we increase the film thickness, tan δ also increases, consistent with this perspective. While thicker films may provide a more accurate quantitative assessment of tan δ, this also conflicts with the goal of measuring the thin film behavior. Future research will consider how to assess the phase angle of the composite to quantify the loss modulus of the thin film. Nevertheless, the KIT method does allow for a quantitative assessment of the storage modulus, which is not possible with the powder clamp and glass-mesh approaches.[1,16] The storage modulus is determined by subtracting the in-phase force−strain response of the substrate from the force−strain response of the composite. The stress is then calculated by dividing the force by the polymer thin film cross sectional area. To assess the accuracy of the storage modulus, we compare the storage modulus at room temperature to E_Y using a film on water (FOW) tensile test (Figure S7).[28] The DMA test was carried out in the linear viscoelastic region (0.2% strain), which ensures that the storage modulus will be roughly equivalent to E_Y. The room temperature E_Y was found to be quite similar to the storage modulus for P3HT, PTB7-TH, PM6 (Figure 3c), and PS (Figure S8). Accurately capturing the storage modulus also provides a means to measure the rubbery plateau modulus, which may be used to determine the entanglement molecular weight of thin polymer films. However, for the case of PS (Figure S8), the rubbery plateau storage modulus is significantly lower than the stiffness and the PI substrate. This lower stiffness coupled with the thin film being characterized makes it a challenge to accurately capture the rubbery storage modulus. As mentioned above, the kirigami pattern used to study PS was purposefully made more rigid to limit PS fracture when loading the glassy thin film. Thus, further optimization of the Kirigami pattern should enable quantitative assessment of the film's rubbery behavior.

We now turn to the thermal relaxation of polymer/small molecule acceptor (SMA) blends used in OPVs. We consider the donor polymer, PTB7-TH, blended with the SMA IEICO-4F, with the molecular structure given in Figure S1. This system has been shown to result in high performance BHJ OPVs with power conversion efficiencies over 12%.[29] PTB7-TH:IEICO-4F, like many OPV material systems have poor miscibility and the blends must be quenched from solution to ensure the materials do not overly segregate, enabling high performance OPV cells.[17] This presents a challenge for DMA measurements as drop-cast samples will have a morphology that is significantly different from the films used in a device. Here, we test the relaxation behavior of spun cast blend films that replicate the device processing conditions using the KIT method and compare it to the drop-cast films tested using the glass-mesh technique. The thermogram of the neat PTB7-TH is compared to blends with IEICO-4F at ratios of 1:1 and 1:1.5 by mass provided in Figures 4 and S9. The films for the KIT tests were between 600 and 650 nm thick, achieved by transferring multiple spun cast films on the PI support. In both test approaches, the addition of the SMA results in suppression of the secondary relaxation at approximately −20 °C to 0 °C, as observed by the drop in the tan δ peak. The suppression of the secondary relaxation increases with the amount of SMA in the blend for the KIT method, as shown in Figure 4c, which is consistent with the SMA acting as an antiplasticizing agent.[30,31] However, this suppression does not follow the same trend when using the glass mesh method, where the suppression is greatest in the 1:1 blend. The lack of SMA loading dependence in the drop cast samples may be associated with the increased segregation of the SMA out of the mixed phase due to the slow drying rate of drop cast solutions. Note that we also observe differences in the relaxation behavior at higher temperatures (>100 °C) that has been attributed to polymer aggregate relaxation.[6,32] In addition to the changes in tan δ, the storage modulus of the films should increase with SMA loading given the higher stiffness of the SMA compared to the polymer. This is clearly observed when using the KIT method and matches E_Y from the FOW tensile tests well (Figure 4c). However, a trend of increasing E' with SMA loading could not be determined with the glass mesh approach. Thus, it is clear that the KIT method is particularly well suited to probe blend films using relevant casting conditions which provide a more accurate and nuanced view of the film thermomechanical behavior.

In conclusion, a new approach was introduced for thermomechanical characterization of thin films that consists of placing a thin film on a kirigami patterned supporting substrate and testing the composite using DMA in a tensile test configuration. The approach was demonstrated to accurately measure the thermomechanical relaxation of a number of polymer and polymer/SMA blend films. The KIT method was compared to the impregnated glass-mesh approach showing similarities and differences. In fact, the KIT method is an evolution of the glass-mesh approach, where a material support is introduced that efficiently transfers the testing load to the material of interest. Furthermore, the KIT method enables the testing of thin films with well-defined thicknesses, cast using methods relevant to a given application, which are OPVs in this case. The approach was shown to be sensitive to polymer films with thicknesses as low as 70 nm. We demonstrate clear differences in the relaxation behavior of neat polymer and polymer/SMA blends based on processing conditions highlighting the value of the approach. For example, we found that the KIT method accurately captured the sub-T_g relaxation suppression and increase in E' with IEICO-4F loading in PTB7-TH, which was not observed with the glass-mesh approach. Thus, we believe this method will be highly beneficial for studying the thermomechanical behavior of polymer thin films and, in particular, polymer blends where processing has a significant impact on film morphology.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.1c00396.

> Molecular structure of all polymers used, experimental procedure, design optimization, comparison of P3HT behavior on KIT and uncut PI substrate, storage, loss modulus, and tan δ of PM6 and PTB7-TH on glass mesh and KIT, and FOW tensile tests of polymers (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by NSF Award Nos. 1554322 and 1728370.

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