Cascading Retro-Diels−Alder Cycloreversion and Sydnone-Maleimide Based Double 1,3-Dipolar Cycloaddition for Quantitative Thermal Cross-Linking of an Amorphous Polymer Solid

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S *Supporting Information*

ABSTRACT: A new approach to polymer cross-linking is investigated using a cascading cycloreversion of a maleimide-furan adduct and a double 1,3-dipolar cycloaddition between a sydnone and maleimide. The cross-linking proceeds quantitatively above 63 °C, despite the polymer possessing no observable glass transition temperature. The resulting polymer network possesses a high thermal stability (>300 °C) due to the irreversibility of the sydnone-maleimide cycloaddition, which releases CO_2 during the cross-linking, driving the reaction. The rigid three-dimensional structure of the bis-maleimide-sydnone cycloadduct produced local free volumes in films, decreasing the dielectric constant of the material.
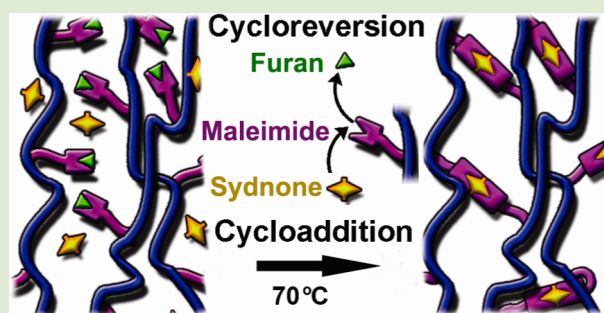
The cross-linking of polymers is a basic chemical process that can profoundly affect the characteristics of the resulting materials, such as their thermal, mechanical, solvent resistance properties, and so on.[1] Cross-linking reactions involving a concerted 6π-electron pericyclic mechanism between two reactants, such as Diels−Alder or Huisgen azide−alkyne cycloadditions, have been studied extensively and are attractive methods, as cross-linking can be achieved in the solid state at reasonable temperatures.[2] These reactions are fairly tolerant of other functional groups, proceed in a clean fashion, without producing unwanted byproducts, and do not require catalysts or cross-linking initiators. As a result, these systems have been adopted for use in a wide range of applications such as self-healing polymers,[3] electro-optic polymers,[4] hydrogels,[5] cross-linked DNA,[6] and drug delivery,[7] to name a few.

While cycloaddition-based cross-linking is versatile, the cross-linking density is limited to less than ∼50% in amorphous solids, which can be attributed to the absence of reaction partners in close proximity.[8] The resulting polymer networks also tend to exhibit limited thermal stability due to cyclo-reversion of the cross-linked adducts at higher temperatures. Generally, the easier the system is to cross-link (that is, the lower the activation energy), the lower the thermal stability is of the resulting polymer network. For Diels−Alder cross-linkable polymers, attempts have been made to improve the thermal stability through modification of the diene and dienophile structures to increase the energy of activation,[4b,9]

with some success, though this lead to the need for high cross-linking temperatures.

In the instance of 1,3-dipolar cycloadditions involving azides, such as the Huisgen azide−alkyne cycloadditions, high-temperature cycloreversion also occurs, which can result in decomposition of thermally unstable addends or produce addends different from the original reactive species.[10]

To tackle these challenges, herein we report a novel cascading retro-Diels−Alder cycloreversion and sydnone-maleimide based double 1,3-dipolar cycloaddition for quantitative thermal cross-linking of an amorphous polymer solid. Sydnones are a class of mesoionic compounds that undergo 1,3-dipolar cycloadditions with a variety of alkenes.[11] The uniqueness of sydnones is in their ability to undergo two consecutive 1,3-dipolar cycloadditions at low temperatures (Scheme 1). The first cycloaddition produces CO_2, driving the

Scheme 1. Double 1,3-Dipolar Cycloaddition between 3-Phenylsydnone and *N*-Phenylmaleimide
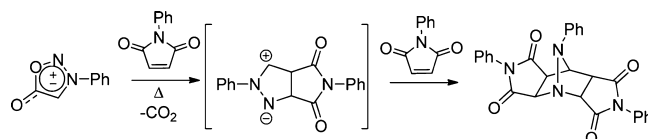
reaction and preventing a reverse reaction. A dipolar reactive intermediate is then formed, which immediately undergoes the second cycloaddition with maleimides. The double reactivity of sydnones, coupled with the high thermal stability of the cycloadduct products (>300 °C), suggests polymers cross-linked with this chemistry should have higher cross-linking density and increased thermal stability over materials made with other cycloaddition cross-linking systems.

To investigate the application of this chemistry for the cross-linking of polymers, we studied the cross-linking dynamics between 3-phenylsydnone and the polymer AJL4, a poly(α-methylstyrene-*co*-N-(4-hydroxyphenyl)maleimide that has had the hydroxy group functionalized with a side chain containing a maleimide-furan adduct (Scheme 2), which we previously

Scheme 2. Cross-Linking AJL4 with 3-Phenylsydnone
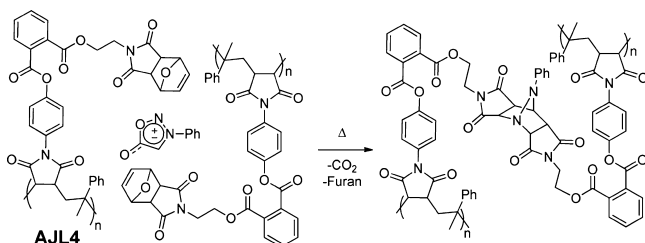
developed as a Diels−Alder cross-linkable system for electro-optics.[12] AJL4 has a furan-maleimide cyclo adduct as a pendant group, which upon heating dissociates to give the reactive maleimide groups. The deprotection proceeds in a very clean fashion and can be achieved at 115 °C in refluxing 1,1,2-trichloroethane without any evidence of thermal cross-linking. Two deprotected maleimides can then react with the sydnone, cross-linking the polymer. Due to the high cycloaddition reactivity of sydnone, the protection of the maleimide side chains in AJL4 was necessary to prevent any pre-cross-linking and facilitate the solution processing of materials.

An AJL4−sydnone composite was prepared by mixing 11 wt % of sydnone (4 mg, 0.025 mmol) with AJL4 (32 mg, 0.050 mmol) in dichloromethane (0.5 mL), which correlates to a 1:2 molar ratio of sydnone to maleimide after the removal of solvent in a vacuum oven. Thermal gravimetric analysis (TGA) of the composite was performed to monitor the loss of CO_2 and furan during the cross-linking process (Figure 1). The composite shows an onset of weight loss at about 62 °C, far lower than the onset of furan loss in neat AJL4. This suggests that the presence of the sydnone catalyzes the dissociation of
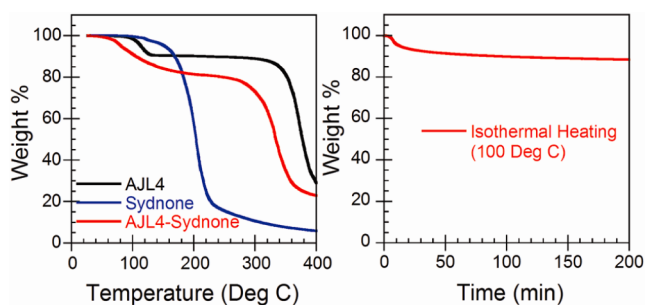

Figure 1. Thermal gravimetric analysis of polymer cross-linking using a 1 °C/min heating rate (left) and using an isothermal heating at 100 °C (right).

the maleimide-furan adduct. Stoichiometrically, the composite of sydnone/AJL4 should display a total weight loss of 12.4% if the cross-linking goes to completion. Surprisingly, a net weight loss of 19.0% was observed in the composite before decomposition of the cross-linked polymer. One possible reason for this unexpected weight loss could be sydnone thermal decomposition, which results in the release of CO_2 and N-methyl-N-phenylhydrazine gases.[13] To see if this was the case, the composite was isothermally heated at 100 °C, well below the 125 °C 2% weight loss temperature of the sydnone. The isothermal heating resulted in a net weight loss of 12.4%, which impressively correlates to a quantitative yield. It should be noted that the composite needs to be dried at room temperature under vacuum to avoid any pre-cross-linking, so residual solvent could have been contained in the TGA sample, artificially inflating the weight loss.

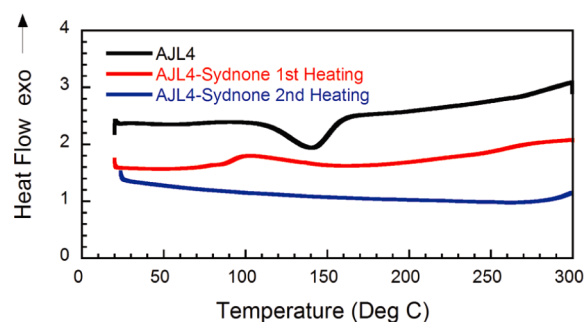Differential scanning calorimetry (DSC) of the composite (Figure 2) shows an exotherm with an onset at 63 °C, in good

Figure 2. Differential scanning calorimetry of AJL4−sydnone composite at a scan rate of 1 °C/min.

agreement with the TGA, and is attributed to the beginning of furan dissociation and sydnone cross-linking. There are no separate endo- and exothermic peaks for the endothermic furan dissociation/evaporation and the exothermic cycloaddition processes. This indicates that furan dissociation and cyclo-addition occur virtually simultaneously. The rate of heat evolution starts out small, as a shoulder of the exothermic peak, but increases dramatically at ~90 °C. The shoulder is likely the result of the endothermic furan dissociation removing heat from the system, while the cycloaddition adds heat. The increase in heat flow after 90 °C can be attributed to the completion of furan dissociation and a high rate of cyclo-addition. The second heating of the cross-linked polymer shows no endothermic transitions below 300 °C. This demonstrates the irreversible nature of the cross-linked adduct, as polymers cross-linked using other cycloaddition reactions show endo-thermic dissociation of the cycloadducts.[4a,c] The irreversibility of the cross-linking combined with the high stability of the resulting cycloadduct lead to a high thermal stability of the polymer network, which the TGA shows is stable up to ~305 °C.

The DSC also shows that the onset of furan dissociation happens at a much lower temperature than that of AJL4, further suggesting that the presence of the sydnone catalyzes furan dissociation. Interestingly, the DSC shows that cross-linking occurs despite the polymer possessing no observable glass transition temperature. The low cross-linking temperature may be due to furan dissociation, which can leave a local free volume

behind as it leaves, giving the sydnone or maleimide enough rotational freedom to react.

To monitor the cross-linking kinetics independently of furan dissociation, a film of the composite was examined using FTIR and UV−vis spectroscopy. The FTIR spectra of the composite (Figure 3) cured at increasing temperatures shows that the peak
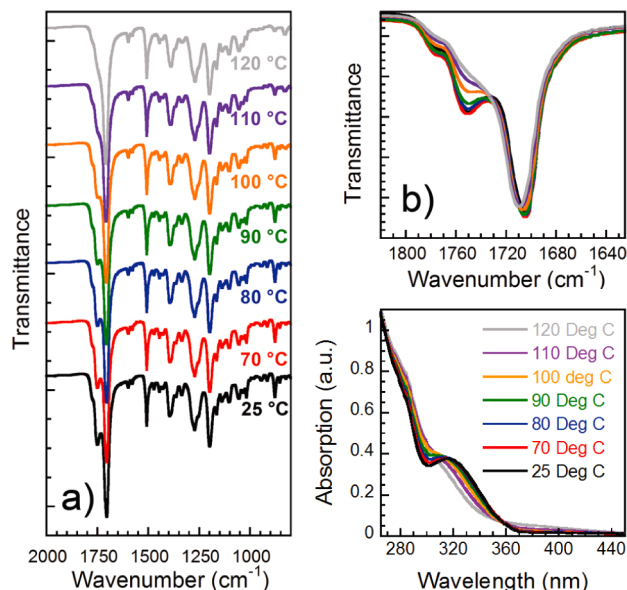

Figure 3. FTIR (a, b) and UV−vis (c) spectra of AJL4−sydnone composite films cured with increasing temperature using 10 min heating intervals.

at 1750 cm^{-1}, attributed to the sydnone carbonyl stretch (see Figure S1 of the Supporting Information), does not change significantly in intensity until the film is heated to 90 °C. This is in contrast to the thermal analysis which shows an onset of cross-linking at 63 °C. It is likely that cross-linking at lower temperatures occurs slowly so that the 10 min heating intervals of the film is not sufficient to see a noticeable change in the sydnone absorption. The composite film did begin to show good solvent resistance at 90 °C, indicating the polymer was cross-linking as the carbonyl stretch decreased. As the curing temperature of the composite was increased, the carbonyl stretch of the sydnone decreased and disappeared completely at 120 °C. Heating the composite at higher temperatures did not lead to a change in the spectrum. As mentioned previously, the high yield of cross-linking found from TGA measurements could be artificially inflated due to trapped solvent in the composite. However, the complete disappearance of the sydnone carbonyl stretch shows that the cross-linking proceeds in a high yield with high cross-linking density.

The UV spectra of the composite are in good agreement with the FTIR spectra. A decrease in the sydnone absorption band at ∼320 nm is seen beginning at 90 °C and continues to decrease until it is cured at 120 °C. The peak at 285 nm, which is attributed to the chromophores in the AJL4 polymer, red-shifts slightly with increased curing temperature. The red-shift is likely the result of the changing environment (polarity and packing) of the chromophores with increasing cross-linking density.

Although the reaction between *N*-phenylmaleimide and 3-phenylsydnone has been thoroughly investigated, the use of a furan-protected maleimide introduces a new variable into this

cycloaddition reaction. The presence of the far less reactive furan-maleimide adduct cycloalkene could potentially react with the sydnone or its intermediate. To investigate if there were any competing side reactions to the cross-linking, a model compound analysis was performed using 3-phenylsydnone (**1**) and a furan-*N*-phenylmaleimide cycloadduct (**2**; Scheme 3). The sydnone and protected maleimide were dissolved in

Scheme 3. Model Compound Reaction of Sydnone with a Furan-Maleimide Cycloadduct
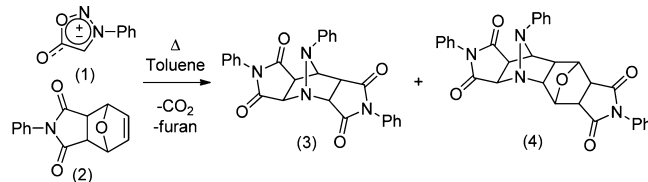
toluene together and heated to either 70 or 100 °C overnight. Liquid chromatography−mass spectrometry (LC-MS) was used to monitor for the presence of small amounts of possible side products. When heated to 70 °C, the expected product **3** was observed, but only as a minor product. Compound **4** was found as the major product with the reaction producing a 28 to 72 ratio of compound **3** to compound **4**. The product resulting from double cycloaddition of the furan-protected maleimide with the sydnone was not observed, which suggests that the sydnone itself will not react with the protected maleimide, but that the highly reactive intermediate formed after the first cycloaddition, can react with it.

When the reaction is run at 100 °C, the ratio between **3** and **4** is changed to 77:23, with compound **1** now becoming the major product of the reaction. The reason for this change in products is that, at lower temperatures, furan dissociation is sluggish and when the sydnone is able to react with the maleimide, a large concentration of protected maleimide is still present to react with. Meanwhile, at higher temperatures, furan dissociation happens quickly and the likelihood of the intermediate reacting with an unprotected maleimide is greater. These results indicate that the composition of the cross-linked polymer could be dependent on the curing temperature. However, if this were the case, a much smaller weight loss in the TGA would be expected because the incomplete loss of furan would add weight to the system. The reason why the sydnone intermediate does not react with the furan-maleimide adduct in the solid state likely is due to the lack of rotational freedom of the sydnone and maleimide. It is not until the furan is removed that the reactive groups possess the ability to orient themselves in a manner that will allow the reaction to proceed.

Due to the outgassing of CO_2 and furan during the cross-linking process, the effects on film morphology were investigated using atomic force microscopy (AFM). Films of the composite were cured at 25, 70, 100, and 130 and were examined for signs of bubbling or porosity. The AFM height images (Figure S2, Supporting Information) show that films cured at 25 and 70 °C have no discernible surface features, with a root-mean-square (RMS) roughness of 1.1 and 1.6 nm, respectively. When cured at 100 °C, however, large bubbles form that are as large as 6 μm in diameter and 20 nm high, with a film RMS of 7.0 nm. The fact that the film cured at 70 °C shows no film bubbles suggests that the CO_2 and furan permeability of the polymer network is greater than the rate of CO_2 and furan evolution. When the rate of gas evolution is

increased at higher temperatures, the gas cannot pass through the film effectively and bubbles are created in the film. Interestingly, when the film is cured at 130 °C most of these bubbles disappear and instead much smaller bubble-like features remain, with a smaller film RMS of 2.9 nm. These surface features may be the remains of bubbles that have collapsed due to the higher temperature and increased rate of gas evolution. An SEM image of one of these surface features (Figure S3, Supporting Information) seems to corroborate this notion as the collapsed bubble has a smooth round base with a rougher top.

To evaluate the effect cross-linking had on the dielectric properties of the AJL4−sydnone composite, the relative permittivity of composite films both uncured and cured were evaluated over a broad range of frequencies. A curing temperature of 70 °C was chosen to avoid any complications arising from the morphological defects discussed previously. Figure 4 shows that there is a small but clear decrease of ∼0.1
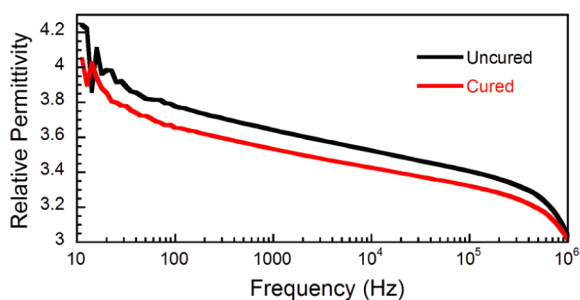

Figure 4. Relative permittivity of AJL4−sydnone composite films as a function of frequency of an AC electric field.

in the relative permittivity of the composite after cross-linking. The 0.1 decrease in the permittivity of the composite is fairly consistent over the 100 Hz to 100 kHz range. The decrease in the permittivity is likely the result of the rigid three-dimensional structure of the cross-link moiety, which has a structure that resembles iptycene, a moiety known to create free volumes in their films when they are integrated into a polymer backbone.[14] While the maleimide-sydnone cycloadduct is less rigid, it clearly creates a local free volume, lowering the dielectric constant of the material. This suggests that sydnone 1,3-dipolar cyclo-addition may be useful in making solution processable dielectric materials, which can be cross-linked to lower the dielectric constant and improve its solvent resistance through post processing curing.

In summary, we have developed a new polymer cross-linking system utilizing the irreversible cycloaddition reaction between sydnone and maleimide, which occurs quantitatively at low temperatures with high cross-linking density. The resulting polymer network possessed high thermal stability and a reduced dielectric constant. This "click" cross-linking approach should be generally applicable to polymer systems previously developed using Diels−Alder or Huisgen cross-linking to increase the cross-linking density.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and additional characterization not included in the manuscript. 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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