SELF-HEALABLE AND RECYCLABLE MATERIALS FROM BIOBASED
POLY(SILYL ETHER)S

BY

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Jigna Parmar

July 17, 2020

List of Abbreviation

PSEs	Poly(silyl ether)s
DA reaction	Diels-Alder reaction
HMF	Hydroxymethylfurfural
BHMF	2,5-Bishydroxymethylfuran
BMI	1,1'(Methylenedi-4,1-phenylene) bismaleimide
DCM	Dichloromethane
DMF	Dimethylformamide
NEMI	N-ethylmaleimide
PSEBMI	Crosslinked (PSEs/BMI)
DMA	Dynamic mechanical analysis
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry

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ABSTRACT

Inspired from natural species that can repair themselves upon injury, a new class of smart materials that fix themselves is of interest. They can repair physical and mechanical damages, thus increasing shelf life and preventing failures. These types of self-healing synthetic thermosetting polymers from renewable resources can help resolve problems caused by using fossil resources, such as environmental pollution, non-recyclability, and non-repairing ability. In addition to the self-healing, the first chapter also presents the Diels-Alder (DA) reaction, the underlying chemistry that helps produce polymers with desirable properties. The simple application of heat in thermosets gives self-healable, recyclable, and reusable materials. In Chapter 2, our research utilizes the diene units in furan-derived poly(silyl ether)s (PSEs) and, it aims to crosslink them by DA reaction with bismaleimide as the DA reaction is an enabling method for self-healing polymers. Preliminary results show crosslinking is feasible with PSEs. DSC and TGA methods are used to analyze thermal properties like stability and reversibility of crosslinked polymers with varying content of crosslinkers. This crosslinked network polymer also shows excellent self-healing ability, recyclability, and degradability.

1.1 Introduction

Thermosetting materials are in high demand due to their excellent thermal stability and mechanical properties. But difficulties in recycling, reshaping, and reprocessing of these materials limit their applications.[1,2] With the increasing consciousness of sustainability, an alternative, emerging subject of recyclable, degradable, and self-healable polymers from renewable resources attracts much interest. The approach produces materials with excellent durability and long life, which is cost-effective and environmentally friendly.[1,2,3,4] One of the properties that make them imperious is the self -healing ability, an ability of the material to heal-itself upon damage.[3,4] It can be classified mainly into two types: extrinsic and intrinsic.[3,4] While the extrinsic systems rely on additional components such as microcapsules, hollow fibers, and vascular approach for delivery of healing agents, the intrinsic self-healing is based on the dynamically reversible bonds built in the network. The covalent bonds include the Diels-Alder (DA) bond, ester exchange, and disulfide exchange, and the non-covalent bond approach consists of hydrogen bonding, metal ion binding, $\pi-\pi$ stacking, and host-guest interaction.[3] Among them, the most investigated approach is the Diels-Alder reaction between a diene and a dienophile. It is feasible to synthesize thermally self-healable and recyclable polymers by incorporating a furan derivative (as a diene) and maleimide (as a dienophile).[5,6] These new classes of polymers also help to strengthen the chemical, mechanical, and thermal properties of the materials.[7]

1.2 Reversible Thermosets

Classical thermosets have been widely used due to properties such as good solvent resistance, excellent thermal stability, and high strength and modulus.[8] However, compared with thermoplastics, they do not melt and are not processable or recyclable. It would be a great

achievement if we can somehow combine the advantages of both the thermoplastics and thermosets. Therefore, reversible thermosets with good healing ability are, particularly of high interest.[9-10] Chen et al. first explored the synthesis of thermosets via the furan and maleimide using the dynamic reversible bond (Diels-Alder reaction).[10-11] After that, Peterson and coworkers made a healable thermoset of epoxy-amine with the pendent furanoic group. As shown in **Figure 1,** the direct addition of the bismaleimide into the cracked polymer gives an accomplishment of a healing
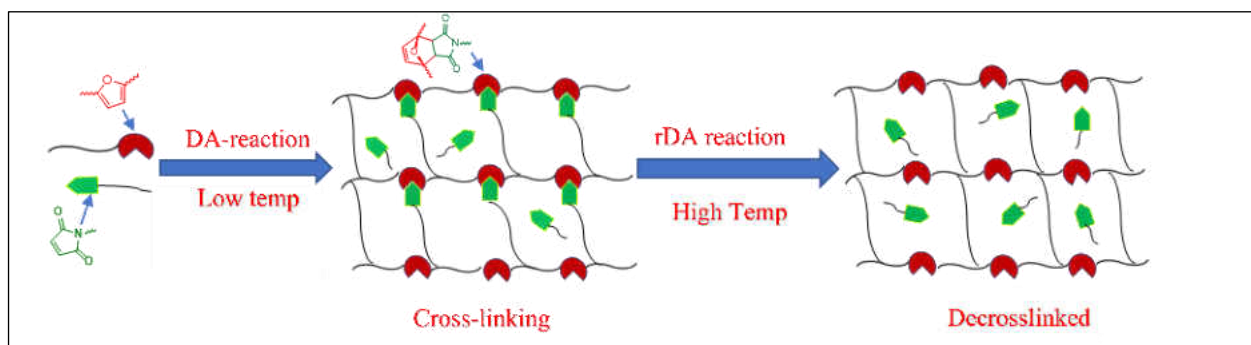
Figure 2. Thermo reversible reaction.

reaction.[12] These fundamental works open the door towards a new class of self-healable thermosets.

1.3 Diels-Alder Chemistry

The Diels-Alder reaction, first discovered by Otto Diels and Kurt Alder in 1928, is the most studied thermally reversible bond chemistry. Specific features like versatility and reversibility at higher temperatures proceed in the absence of the catalyst make it accessible in the production of several organic and inorganic synthesis.[13,14,15] In this [4 + 2] cycloaddition reaction electron-rich diene and electron-deficient dienophile give adducts.[14, 16] (**Scheme 1.**).

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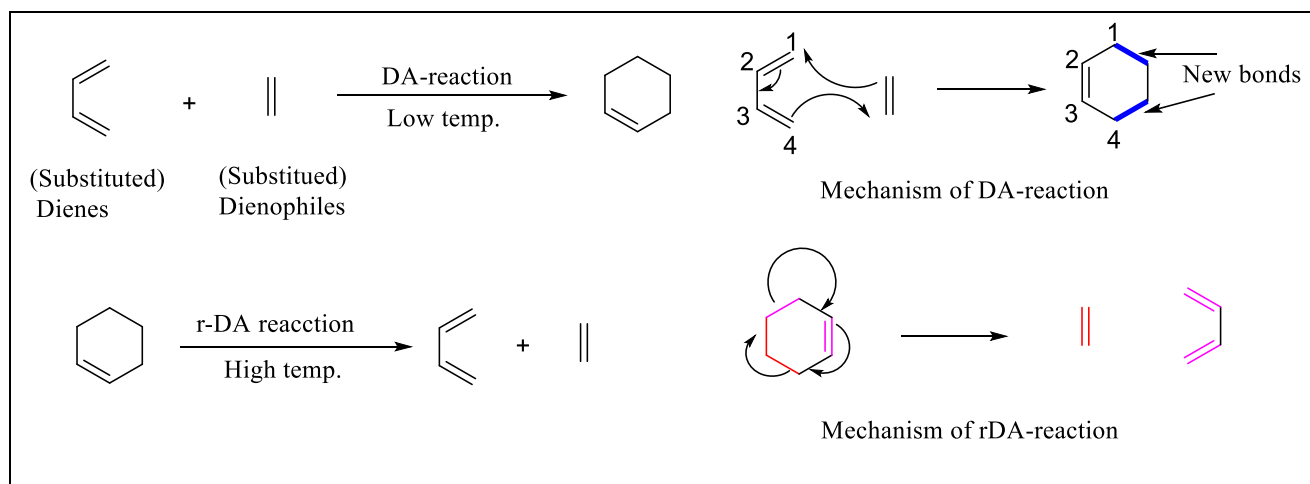
Scheme 1. (a) DA and r-DA Reaction. (b) Mechanism of DA and r-DA Reaction.
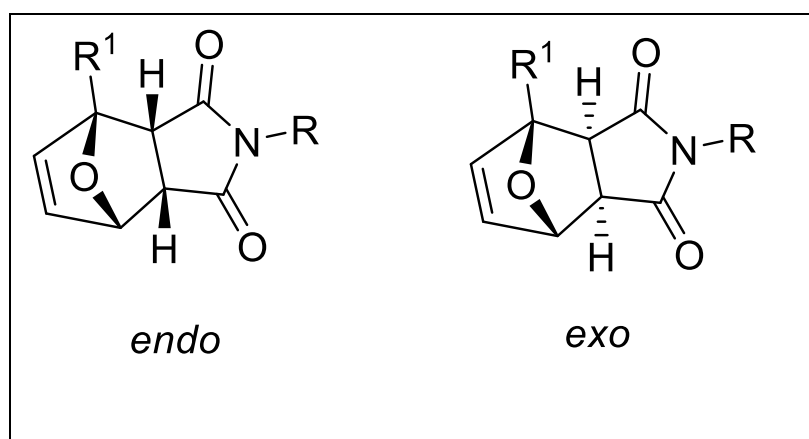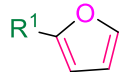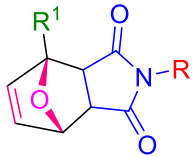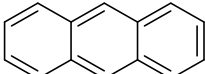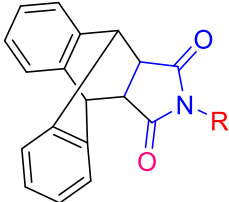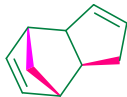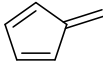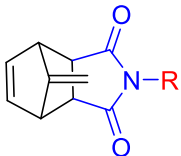
Scheme 2. Structure of Endo and Exo isomers.

This cycloaddition reaction is an exothermic reaction which is governed by the temperature as an external stimulus.[13] DA adduct is predominating at lower temperatures (<100 ^{0}C) while the thermally reversible (retro-DA) reaction) occurs at a higher temperature (>100 ^{0}C). The temperature range of the DA and r-DA reaction depended on the structure of the diene and dienophile. DA reaction gives two isomeric products, *endo* and *exo* isomers. The *endo* is a kinetic product, while the *exo* is a thermodynamic product.[17] (**Scheme 2**)

Various Diels-Alder systems studied in the production of the thermosets are as follows. **Table 1**. represented the overview of the most studied Diels-Alder reaction in literature.[1, 18-22.]

Table 1. Examples of most studied DA-reaction.

Diene	Dienophile	DA-Adduct
Furan	Maleimide	
Anthracene	Maleimide	
Cyclopentadiene	Cyclopentadiene	
Fulvene	Maleimide	

1.4 Self-Healing

Nature provides us an excellent platform for learning. Self-healing is a concept inspired by the natural being that can heal or repair themselves.[15] By mimicking that, researchers are able to make a material that can reform or improve itself upon damage. Self-healing is briefly classified into several classes, as shown in **Figure 2.** [15,16] Among all classes, self-healing via Diels-Alder

reaction is preferable. The thermosets synthesized via this reversible reaction can be readily controlled with temperature. The resulting polymer may have a unique dynamic and mechanical properties.[23] Reusable and remendable materials with several repeatabilities upon damage also can be achieved by this reaction.
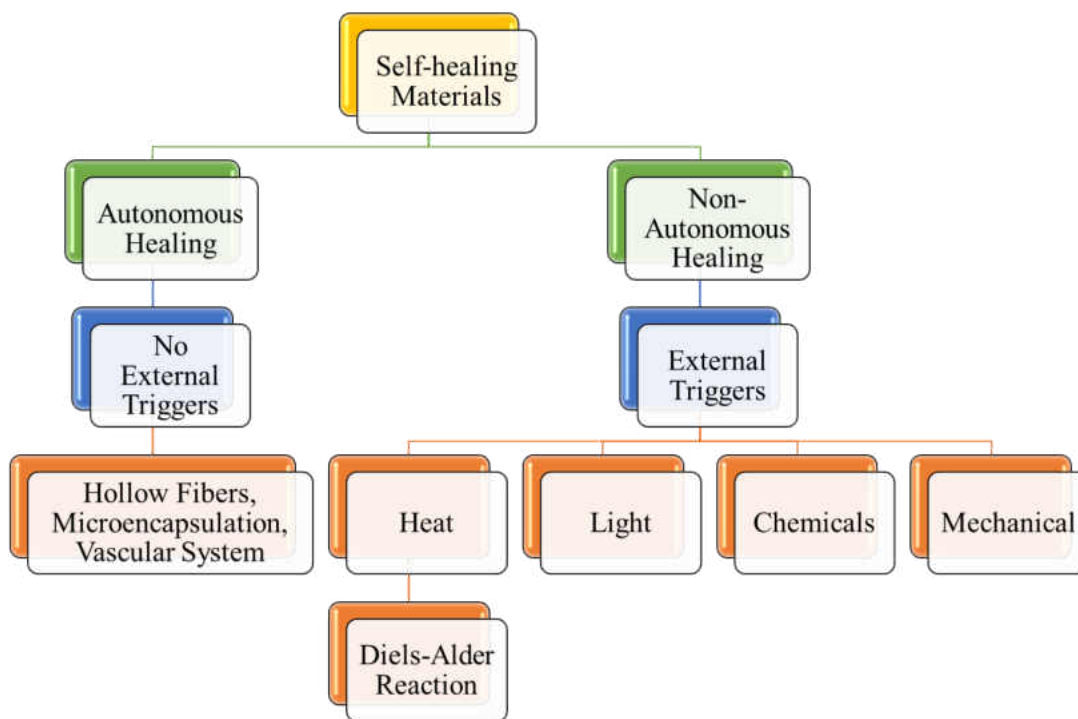
Figure 3. Classification of Self-Healing.
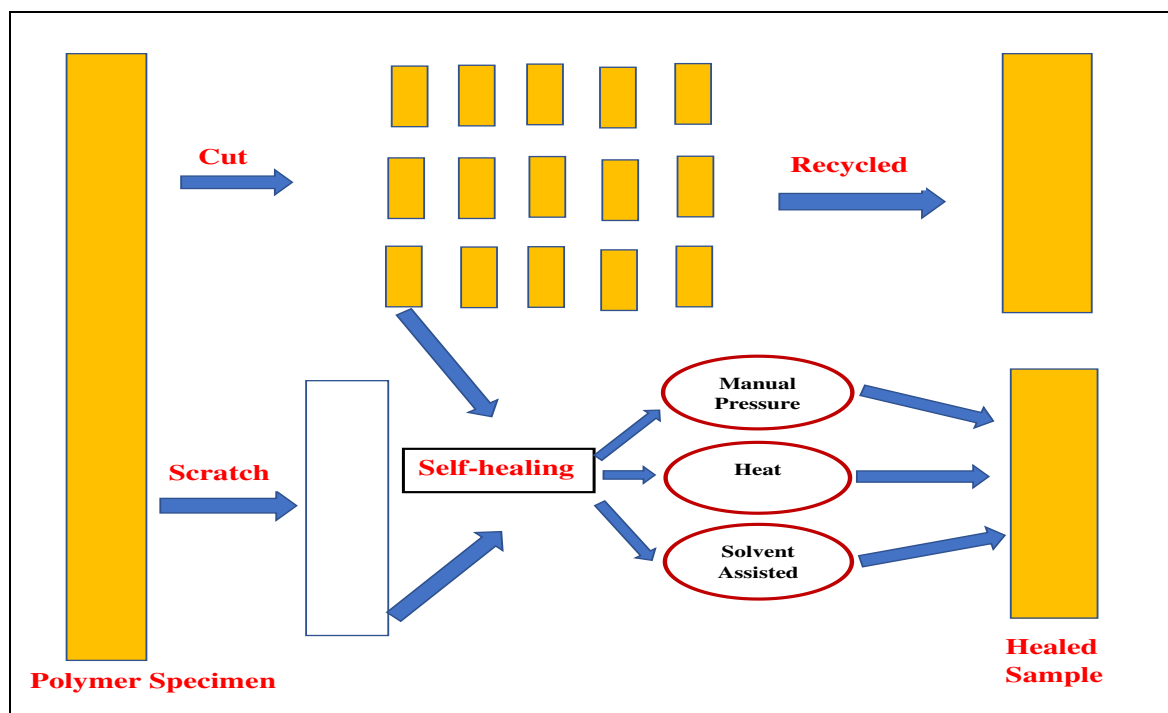
Figure 4. General Methods for Self-Healing and Recyclability.

As shown in **Figure 3**, recyclability and self-healing can be performed in both cuts and scratched samples. When the polymer surface is scratched or cut, the healing is possible via the Diels-Alder mechanism. It can be achieved by manual pressure, the application of the heat, as well as with the use of a small amount of solvents like DCM, DMF, etc.[22, 24]

1.5 2,5-Bis-(hydroxymethyl)furan (BHMF)

Petroleum resources are non-renewable and could cause environmental pollution. In contrast, sustainable materials from renewable resources are abundant and cheap and provide an excellent platform for various synthesis of building blocks. BHMF is an important diol derived from biomass. It is mainly used as a monomer to synthesize different materials like polyesters, polyurethane, poly(silyl ether)s, crown ethers, and esters.[25-27] BHMF is generally derived from 5-hydroxymethylfurfural (HMF). HMF is a dehydrated product of glucose and fructose.[26] Here a few selected examples of the synthesis of BHMF are shown in **Scheme 3**.[25-27]

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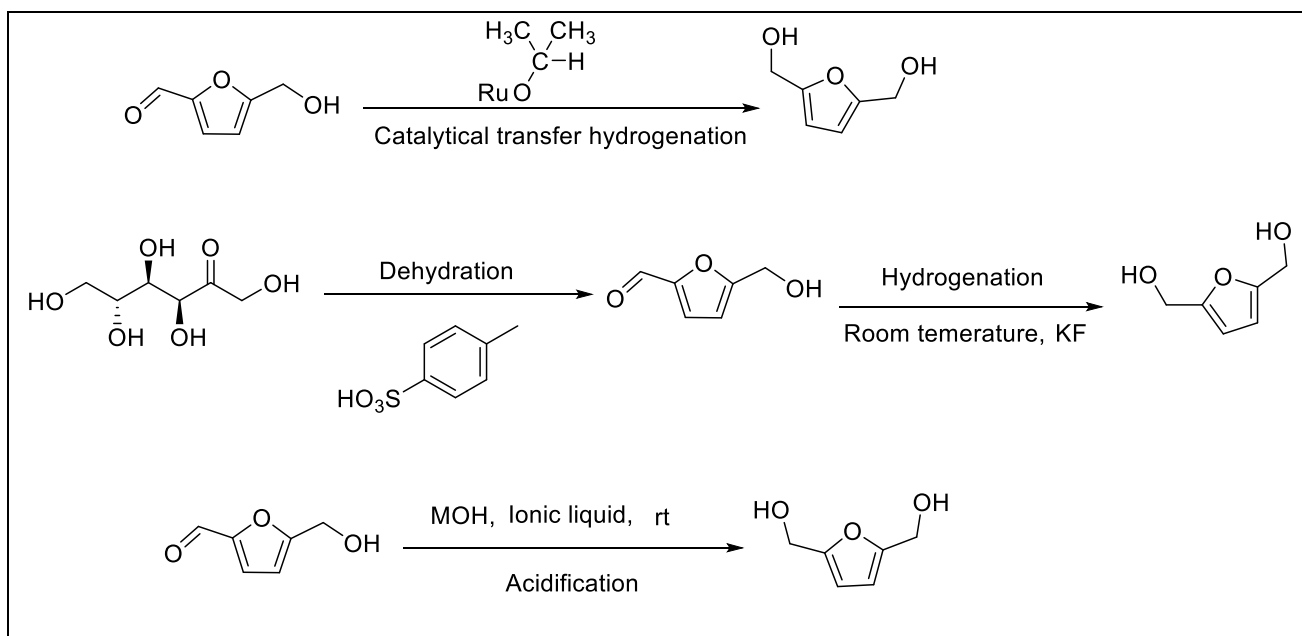
Scheme 3. Different Methods to Synthesized BHMF.

1.6 Poly(silyl ether)s (PSEs)

Poly(silyl ethers) are one of the promising, robust materials. The Si−O−C linkage present in the PSEs provides good degradability via acid-base hydrolysis,[29-31] in contrast with the Si−O−Si bond in polysiloxanes.[28-30] Properties such as excellent thermal stability at a higher temperature, lower glass transition temperature, and biocompatibility make them a worthy subject for research. PSEs are useful for the preparation of organic and inorganic hybrid polymers materials.[30] PSEs also are used in many applications such as biomedicals, column packaging, and coating.[28-30]

Various synthetic routes have been used to synthesize PSEs. The most popular ways are via condensation polymerization, typically between diols and dihydrosilanes, diamino or alkoxysilanes, and dichlorosilanes.[29] Below are a few syntheses (**Scheme 4.)**

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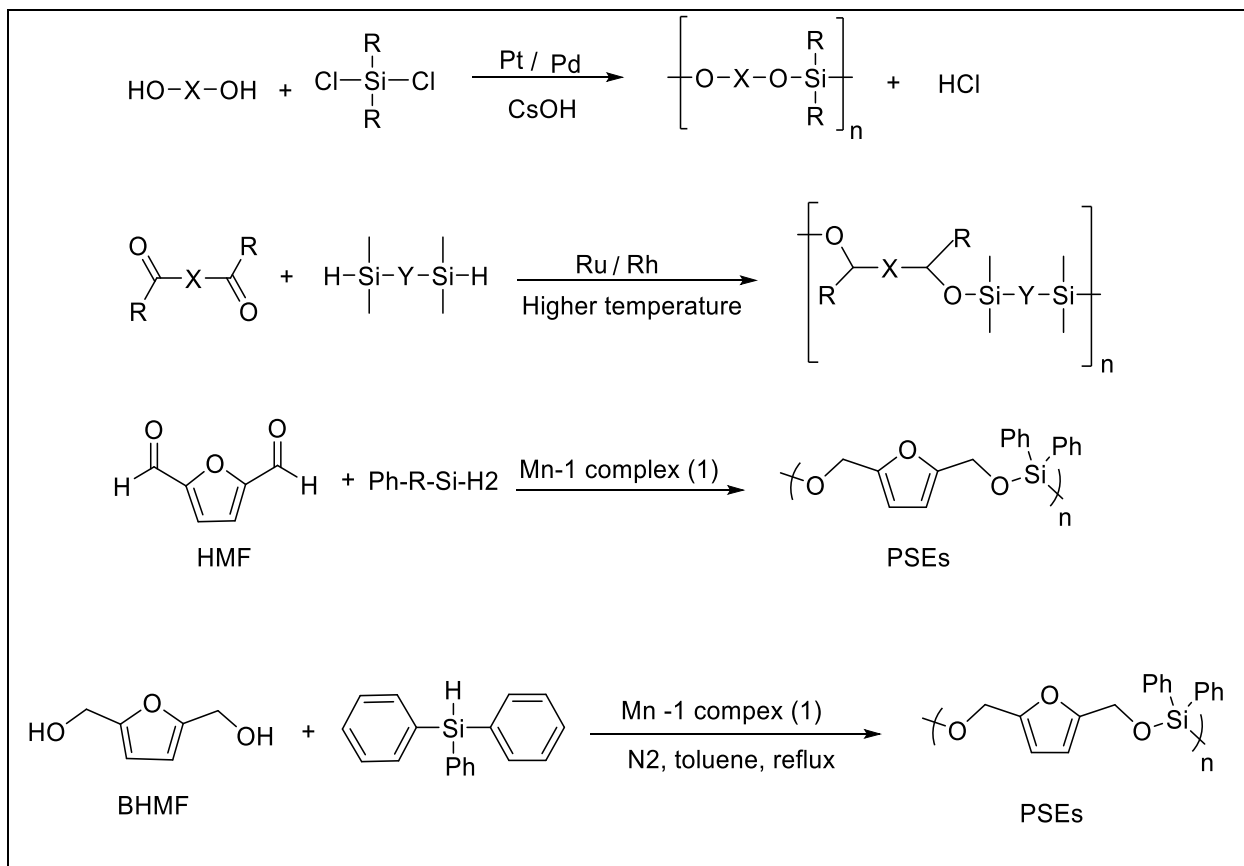
Scheme 4. Various Examples of Synthesis of PSEs

1.7 Bismaleimide (BMI)

Bismaleimides are typical crosslinkers in the Diels-Alder chemistry. Our project is also based on the Diels-Alder reaction between furan and bismaleimide. We aim to make a self-healable, recyclable crosslinked polymer by using a furanic group-containing polymer and a bismaleimide as a crosslinker. Bismaleimides are electron-deficient dienophiles, and furanoic compounds are excellent electron-rich dienes. Maleic or acetic anhydride and an amine are the primary sources to synthesize the bismaleimide.[32,33] **Scheme 5** below sported a few syntheses of BMI.

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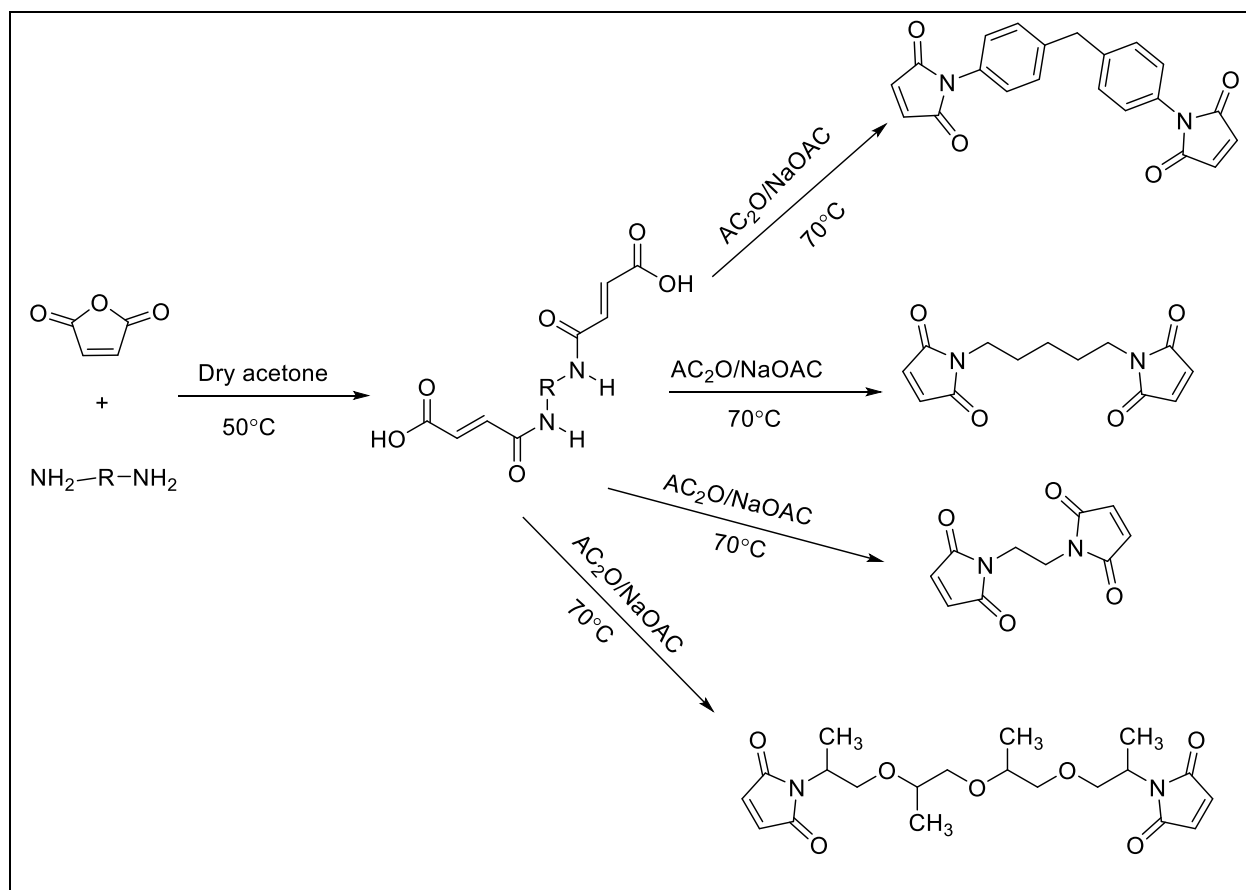
Scheme 5. Synthetic Methods to Different BMIs.

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2.1 Introduction

Petroleum-based materials, widely used today, are from nonrenewable resources and unsustainable. An alternative is bioderived materials that are abundant, renewable, inexpensive, and environmentally safe.[1,2,3] The exploration and use of such materials open a new era in the field of research. An excellent example is a class of furan-based molecules. Furanic compounds are derived from agriculture waste and renewable resources like corn husks, wheat straw, and sugarcane waste.[4] Various new thermosets and thermoplastics, such as polyesters, polyurethanes, and poly(silyl ethers), have been derived from furan and their derivatives. [5,6,7]

The use of natural resources will help to achieve sustainability. It may also increase the lifecycle of the thermosets, which is a major limitation of traditional thermosets. The properties such as recyclability, processability, and self-healing can be achieved via dynamic bond exchange reactions such as Diels-Alder reaction, trans-esterification reaction, host-guest interaction, and disulfide exchange reaction.[5] Among them, the most promising approach is the DA-reaction because of its ability to promote the crosslinking at low temperature in a variety of polymers.[8] Crosslinked polymers formed by this technique give thermally reversible, recyclable, and self-healable thermosets. Craven first made a thermoreversible crosslinked polymer via DA reaction using the condensation polymerization reaction.[9] In this reaction, he used pendent furanoic group material and maleimide as a crosslinker. Chen et al. utilized this approach and synthesized a healable furan/maleimide network structure.[10]

2.1.1 Poly(silyl ether)s

PSEs are a new class of degradable and partially renewable polymer with remarkable properties.[11,12,13] Silyl ethers help to provide excellent thermal stability and good mechanical

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properties into a polymer network. At the same time, the incorporation of the labile Si−O−C linkage enables them to degrade easily via acid or base hydrolysis.[11,12,13] In addition, the self-exchange reaction of silyl ethers can lead to vitrimers that offer durability and processability in crosslinked polymers.[7]

In this study, our work is based on the furan-derived degradable PSEs and aims to crosslink them by the DA reaction with bismaleimide. The furan-functionalized PSEs were prepared from furan-based monomer 5-hydroxymethylfurfural (HMF) or 2,5-bis(hydroxymethyl)furan (BHMF) with Ph$_2$SiH$_2$.[5] The crosslinking of PSEs carried out with 1,1'-(methylenedi-4,1-phenylene)bismaleimide via DA reaction.[14-21.] The retro-DA reaction and the hydrolysis of synthesized polymers were performed as well. The thermal properties investigated via DSC/TGA techniques. Finally, the self-healing of the network polymer PSEBMI was demonstrated by different healing methods.

2.2 Experimental Section

2.2.1 Materials

The deuterated chloroform (CDCl$_3$) and dimethylsulfoxide (DMSO-d$_6$) were purchased from the Cambridge Isotope Laboratories. 1,1'-(Methylenedi-4,1-phenylene) bismaleimide (BMI) and N-ethylmaleimide(NEMI) were purchased from MilliporeSigma, and 2,5-bis(hydroxylmethyl)furan (BHMF) was purchased from Combi-Blocks, Inc. (CA, USA). The poly(silyl ether)s used synthesized according to the literature procedure (M_n = 7300 g/mol).[14]

2.2.2 Methods

The spectra of ^{1}H and ^{13}C NMR were recorded on a Bruker AVANCE 500 NMR spectrometer with tetramethylsilane (TMS) as an internal reference. The FT-IR was accomplished on a Thermo Scientific Nicolet iS5 FT-IR instrument and analyzed with OMNIC 8.2 software. The

analysis of the sample was carried out by loading it directly with no support on an iD5 ATR accessory. The differential scanning calorimetry (DSC) was performed by using a PerkinElmer Jade differential scanning calorimeter with pyris V9.0.2 software. The zinc and indium standards were used to calibrate the instrument. The samples analysis was carried out by using hermetic pans under the nitrogen atmosphere (flow rate 20 mL/min) with a heating range of -30 to 160 °C. The thermogravimetric analysis (TGA) was performed on an SDT Q 600 instrument accompanied by the Advantage Software. The TGA data were analyzed by using the second heating cycle. The samples were heated in alumina (Al_2O_3) cups from 30 to 800 °C with a heating rate of 20 °C/min with N_2 (furnace purge gas) at a flow rate of 100 mL/min.

2.2.3 Synthesis of DA-Adduct of BHMF/BMI (3)

In a 100 mL round bottom flask equipped with a magnetic stirrer, the BHMF (100.0 mg, 0.78 mmol) and BMI (139.8 mg, 0.39 mmol) were added in the molar ratio of 2:1, followed by 50 mL of dichloromethane (DCM). The reaction mixture (light yellow in color) was placed in a pre-heated oil bath at 30 °C for 24 h with constant stirring. Precipitation started to form after a few minutes in the reaction mixture. The reaction progress was monitored periodically with ^{1}H NMR spectroscopy by taking out a small amount of the sample. The reaction mixture was filtered, and the filtrate was placed in a beaker and dried under the fume hood for two days to yield **3** (55%) as a pale-yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6, δ-ppm): 7.29−7.37 (m, 8H, aromatic), 7.23−7.32 (d, 4H, aromatic), 7.03−7.15 (d, 4H, aromatic), 6.47−6.56 (d, 2H, −CH=CH−, furan), 5.20 −5.22 (s, 2H), 4.35 (m, 4H) 4.03 (s, 2H) 3.38 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6, 298 K, δ-ppm): 174.33−174.89 (4 C=O), 141.72(CH=CH, 4C), 136.45 (4C, aromatic), 135.00 (2C, aromatic), 130.39 (4C, aromatic), 127.28 (4C, aromatic), 91.31−92.92 (4C), 59.49-60.08 (−CH_2O, 4C), 51.06 (−CH_2, 2C), 47.62 (−CH, 4C).

2.2.4 Synthesis of PSEs/NEMI (6) Using DA-Reaction

PSE (97.7 mg, 0.295 mmol of furan units) and NEMI (59.6 mg, 0.443 mmol of maleimide units) mixed in the equivalent molar ratios of 1.0:1.5 and dissolved in 50 mL of DCM in a 100 mL round bottom flask. The flask was placed in a pre-heated oil bath at 35 °C with a magnetic stirrer. The ^{1}H NMR used to monitor the reaction progress periodically. After 48 hours, the reaction stopped, and the solvent was stripped off. The light yellowish crude product was dissolved in a 1-2 mL of DCM, followed by portion-wise addition of 10-12 mL of methanol. The precipitate obtained was filtered, and vacuum dried. [5] The percentage yield of the product was 70 %. ^{1}H NMR (500 MHz, CDCl$_3$, δ-ppm): 7.62−7.66 (m, 8H, Ph), 6.64−6.04 (d, 2H, −CH=CH−), 5.67−5.64 (s, 2H), 4.75−4.62 (s, 2H), 3.33 (m, 2H), 1.27 (t, 3H), ^{13}C {1H} NMR (125 MHz, CDCl$_3$, 298 K, δ-ppm): 169.67 −173.85 (C=O), 130.57-134.60 (CH=CH, aromatic), 56.85−60.73 (OCH$_2$), 46.58 (CH), 32.22−31.76 (N −CH$_2$),12.88 (CH$_3$).

2.2.5 Synthesis of Crosslinked Polymers PSEs/BMI (PSEBMI) (7) via DA Reaction

Table 2. Different ratios of PSE/BMI Samples.

SAMPLE	$I_{Fu/Ma}$ (ratios)	PSE (mg)	BMI (mg)
PSEBMI-1:1.5	1:1.5	440.8	384.2
PSEBMI-1:1.25	1:1.25	156.1	113.6
PSEBMI-1:1	1:1	466.4	270.6
PSEBMI-1:0.75	1:0.75	862.6	376.3
PSEBMI-1:0.50	1:0.5	343.4	96.8
PSEBMI-1:0.25	1:0.25	596.5	82.4

For the preparation of crosslinked polymers, PSE and BMI were mixed in a 100 mL round bottom flask, with different molar ratios of the furan and maleimide units, Fu/Ma = 1:0.25, 1:0.50, 1:0.75, 1:1, 1:1.25, 1:1.5 (**Table 2**). 50 mL of DCM added into the flask. Then the round bottom

flask place at 40 °C with constant magnetic stirring in a preheated oil bath. The FTIR spectroscopy used periodically to monitor the reaction progress. After 48 hours, the reaction stopped. The solvent was removed by using a rotavapor. The percentage yields with different ratios of PSEBMI products are in the range of 80.0−88.0 %. In the FT-IR spectroscopy analysis of the PSEBMI (**Figure 12**) the appearance of a Si−O−C at 1260 cm^{-1} and C=O group absorption band at 1711 cm^{-1} and the disappearance of the characteristics absorption band of maleimide groups at around 829 and 687 cm^{-1} confirmed the PSEBMI product formation.[11,25]

### 2.2.6 Preparation of Crosslinked PSEBMI Specimen

The preparation of the specimen is a crucial part of self-healing and recyclability testing. To cast the crosslinked polymer film, the different molar ratios of Fu/Ma were used. First, PSEs and BMI were dissolved separately in DCM (20 mL each) in beakers, then they were mixed in a round bottom flask. The round bottom flask was heated at 40 °C in a preheated oil bath with stirring. The reaction was monitored periodically by IR. After 12 h, a pale-yellow solution was transferred into the beaker and heated at 50 °C in a fume hood. After all the solvent was evaporated, the viscous light yellow or brownish materials were quickly transferred into a silicone mold. The cast specimen was taken out from the mold after 48 h.

2.3 Results and Discussion

2.3.1 Model DA Reaction

To explore the feasibility of the reaction and to better understand the thermal behaviors of crosslinked PSEs (**7**), two different models of DA-adducts were first synthesized. The first model reaction is between two small molecules, BHMF and BMI (**Scheme 6**). The ^{1}H NMR of the isolated product (**3**) is shown in **Figure 4**. The adduct formation is confirmed by the characteristic peaks at 6.47−6.56 ppm, assigned to the CH=CH of the DA adduct; the appearance of the two

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peaks can be attributed to the presence of *endo* (6.47 ppm) and *exo* (6.56 ppm) isomers, with the *endo* isomer as the major product. The assignment is corroborated with the methine CH peaks at 3.14 and 3.64 ppm, which can be attributed to the *exo* and the *endo* isomer, respectively.[22] In ^{13}C NMR (**Figure 5**), the methine carbon signal of the DA-adduct around at 47.62 ppm was in agreement with the expected reaction. The FT-IR spectrum (**Figure 6**) shows the OH absorption band at ~3392 cm^{-1} and the C=O absorption band at ~1706 cm^{-1}, consistent with the expected product (**3**). In addition, the characteristics absorption peaks of maleimide at around 829 and 689 cm^{-1} almost disappeared in the crosslinked product, indicative of the progress of the DA reaction.
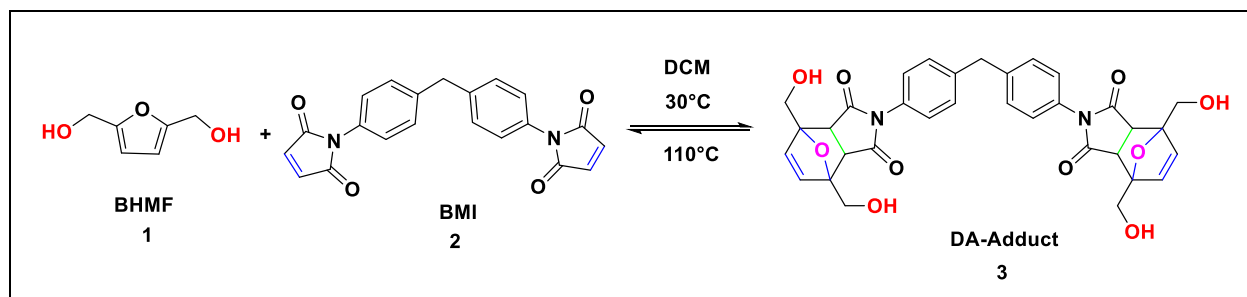
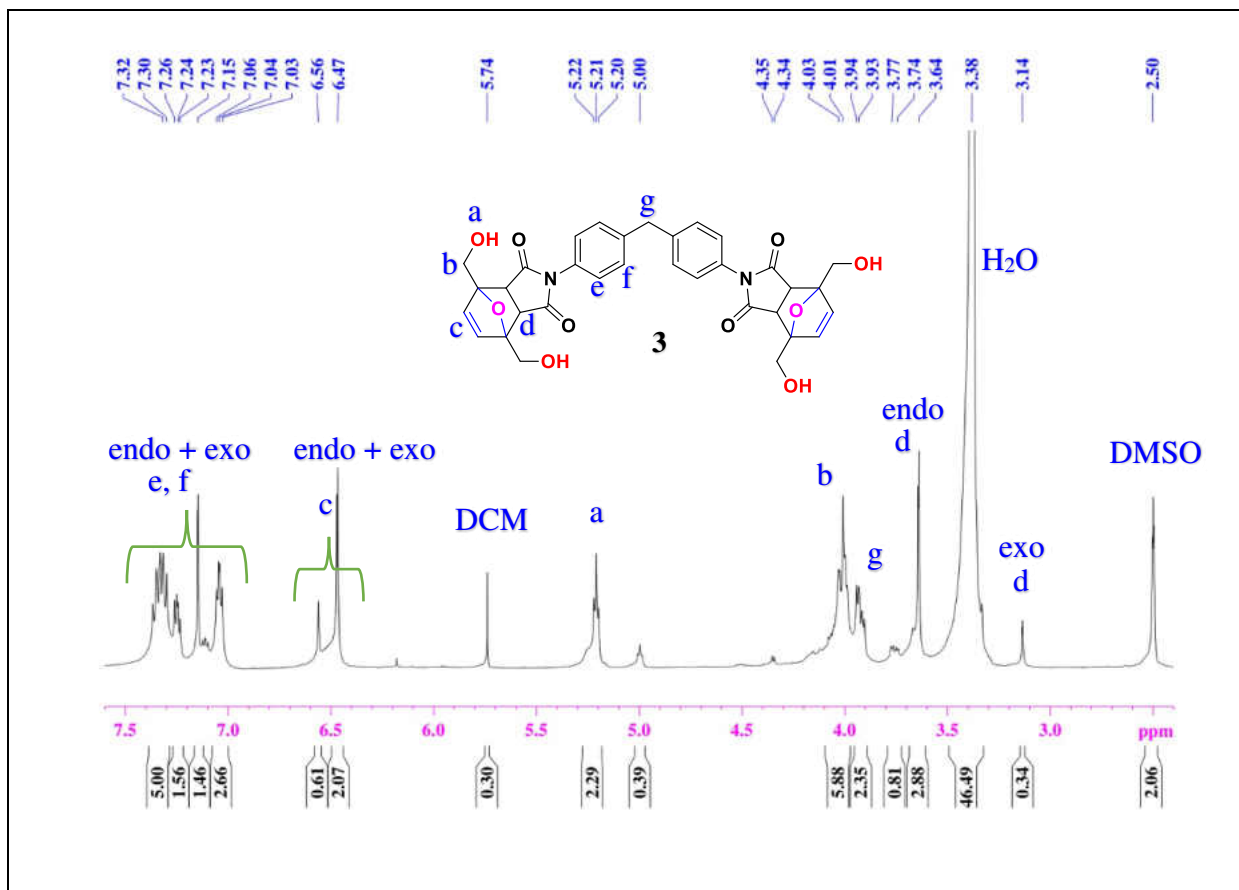**Scheme 6**. Synthetic Routes for the Preparation of BHMF/BMI-DA-Adduct.

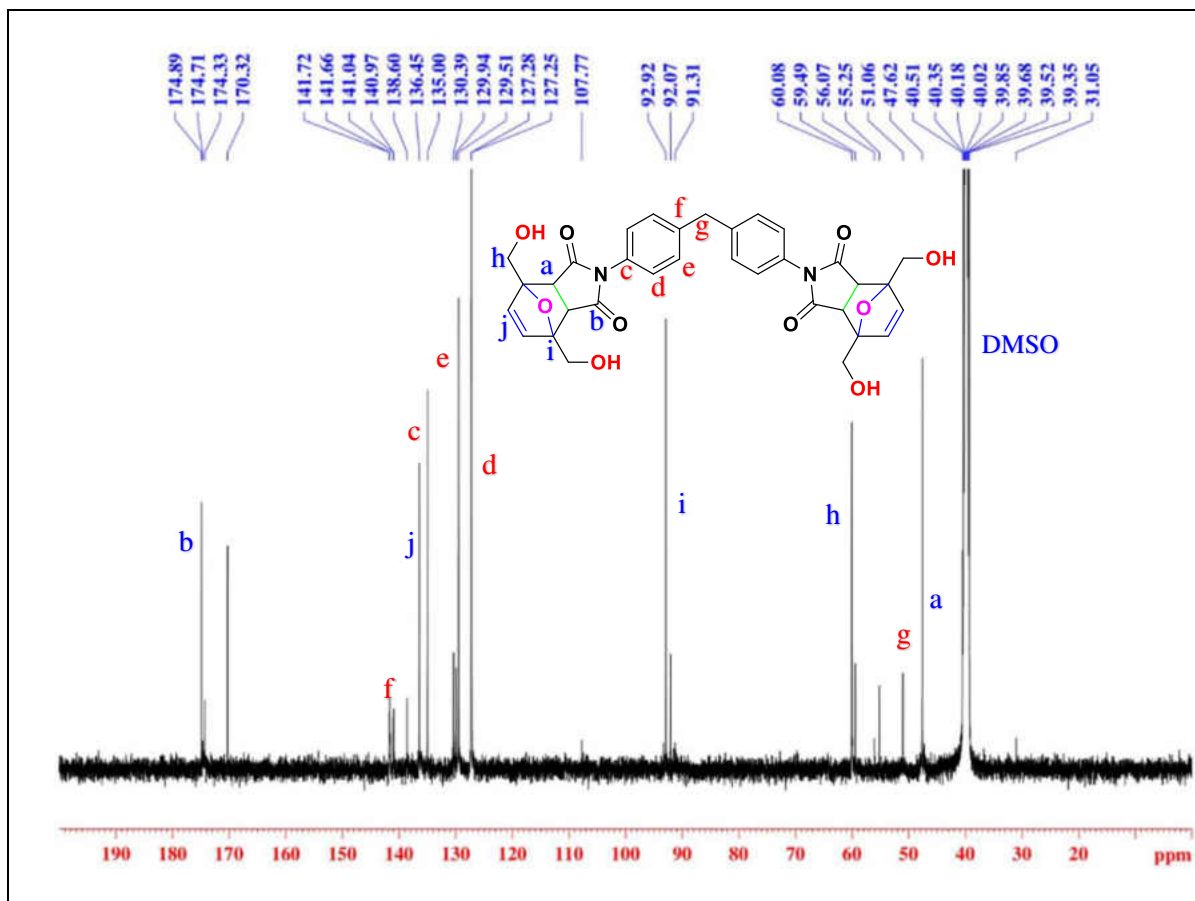**Figure 5.** ^{1}H NMR of DA-Adduct of BHMF/BMI in DMSO-d_6.

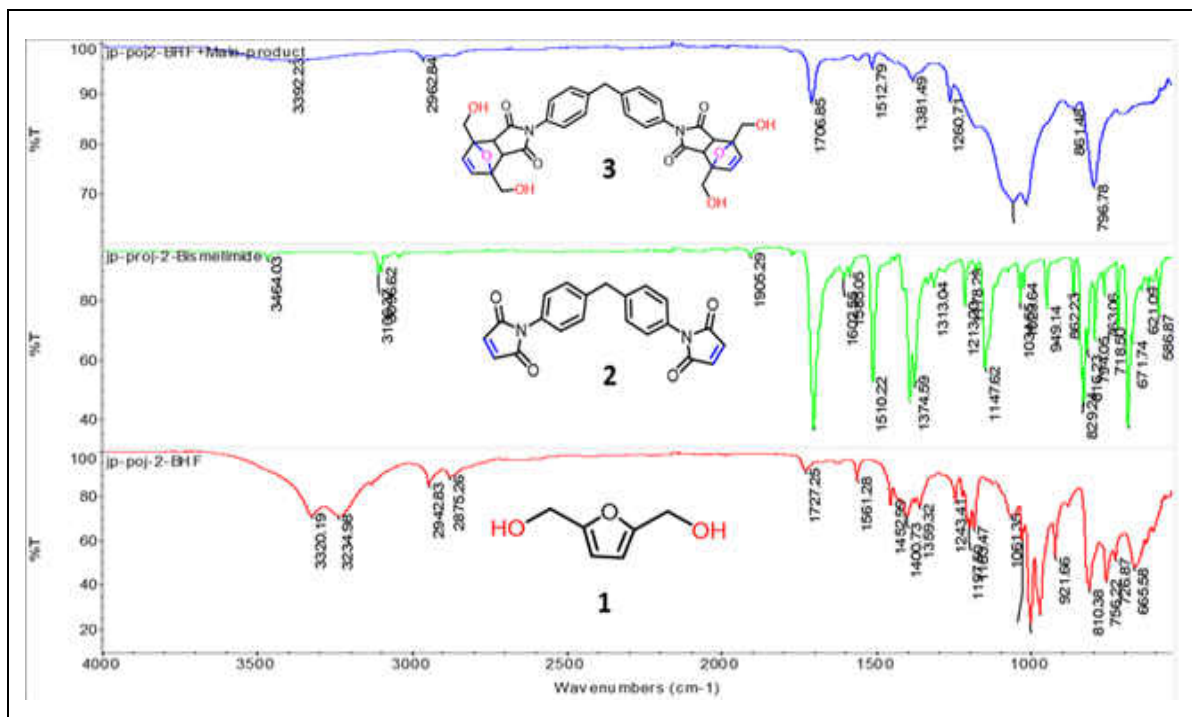**Figure 6.** ^{13}C NMR of DA-Adduct of **3** in DMSO-d$_6$

Figure 6. Comparison of the DA adduct with substrates using IR Spectroscopy.

The second model reaction is between a furan-based PSEs (**4**) and a simple maleimide NEMI (**5**) (**Scheme 7**). The ^{1}H NMR of the product (**6**) is shown in **Figure 7.** Peaks at 6.04−6.23 ppm represent the CH=CH hydrogen of the furan ring, and an appearance of the new peak of CH at 3.56 ppm is the indication of the product formation. In ^{13}C NMR (**Figure 8**) peaks at 46.52 ppm of the methine carbon and 56.85−60.78 ppm of CH_2O peaks are the confirmation of the product. The C−H and H−H correlation from the 2D NMR also support the assignment as the desired product (**Figure 9** and **Figure 10**, respectively). The band at 1260 cm^{-1} in the FTIR spectrum (**Figure 11**) represents the Si−O−C linkage, and a band around 1700 cm^{-1} confirms the C=O absorption. These two bands indicate the synthesis of the product (**6**). In addition to that, the maleimide group (CH=CH) characteristics absorption bands at around 689 and 829 cm^{-1} getting disappeared as DA-reaction progress. That further confirmation of the DA-adduct (**6**) formation.
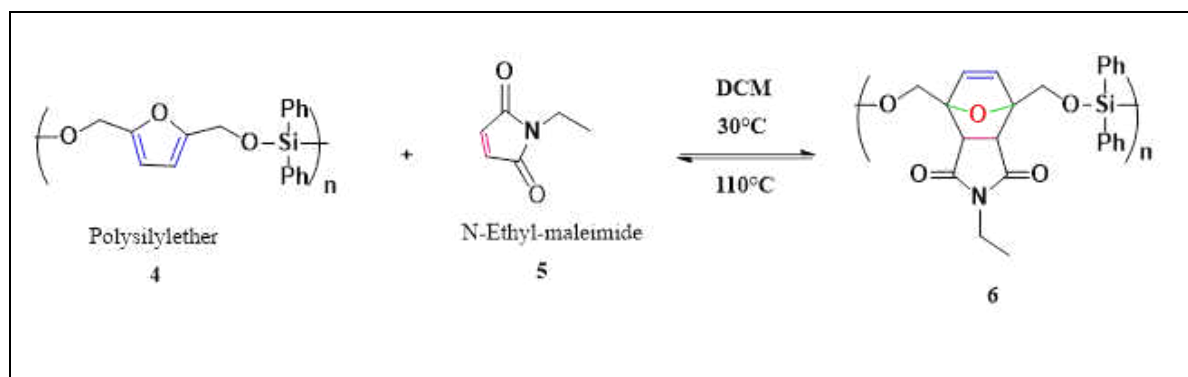
Scheme 7. DA-Adduct of PSEs/NEMI.
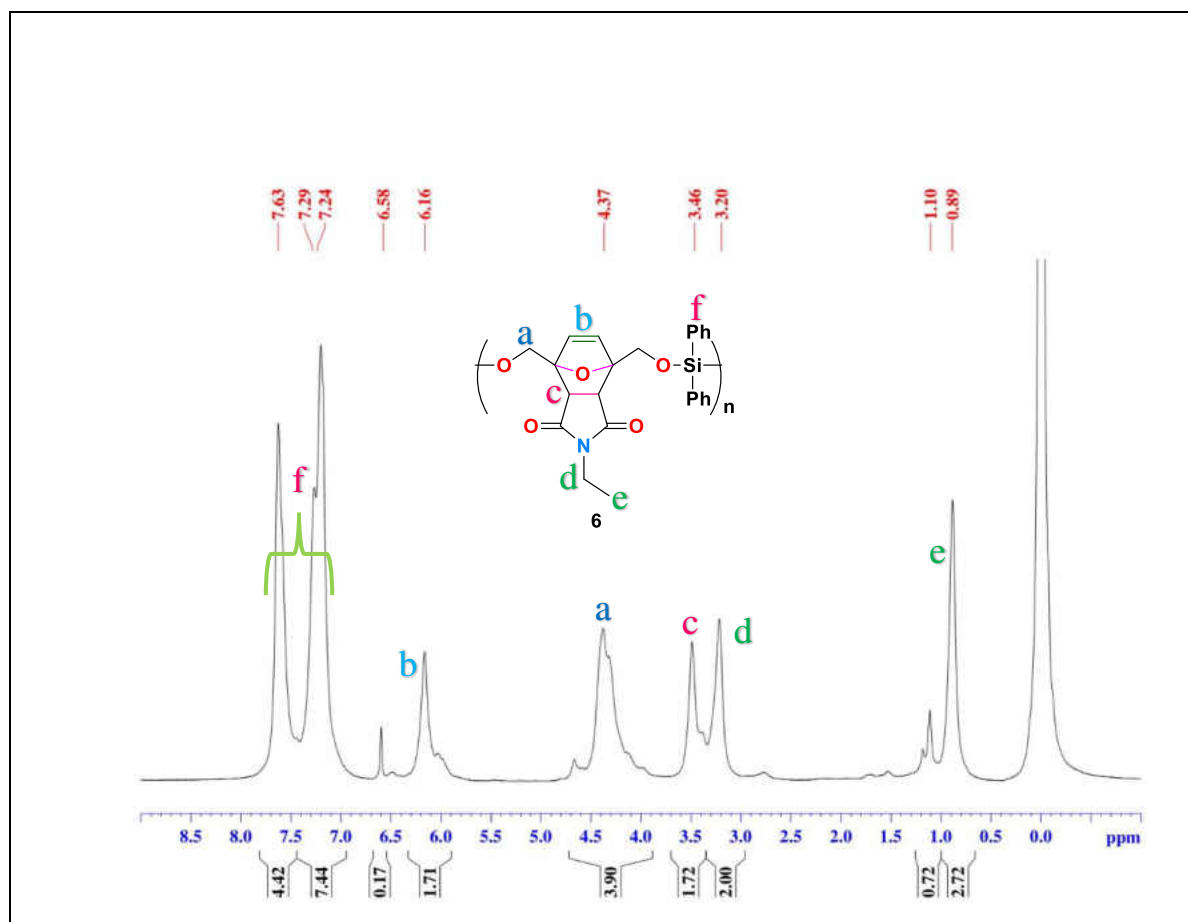
Figure 7. ^{1}H-NMR of PSEs/NEMI Adduct in CDCl$_3$.
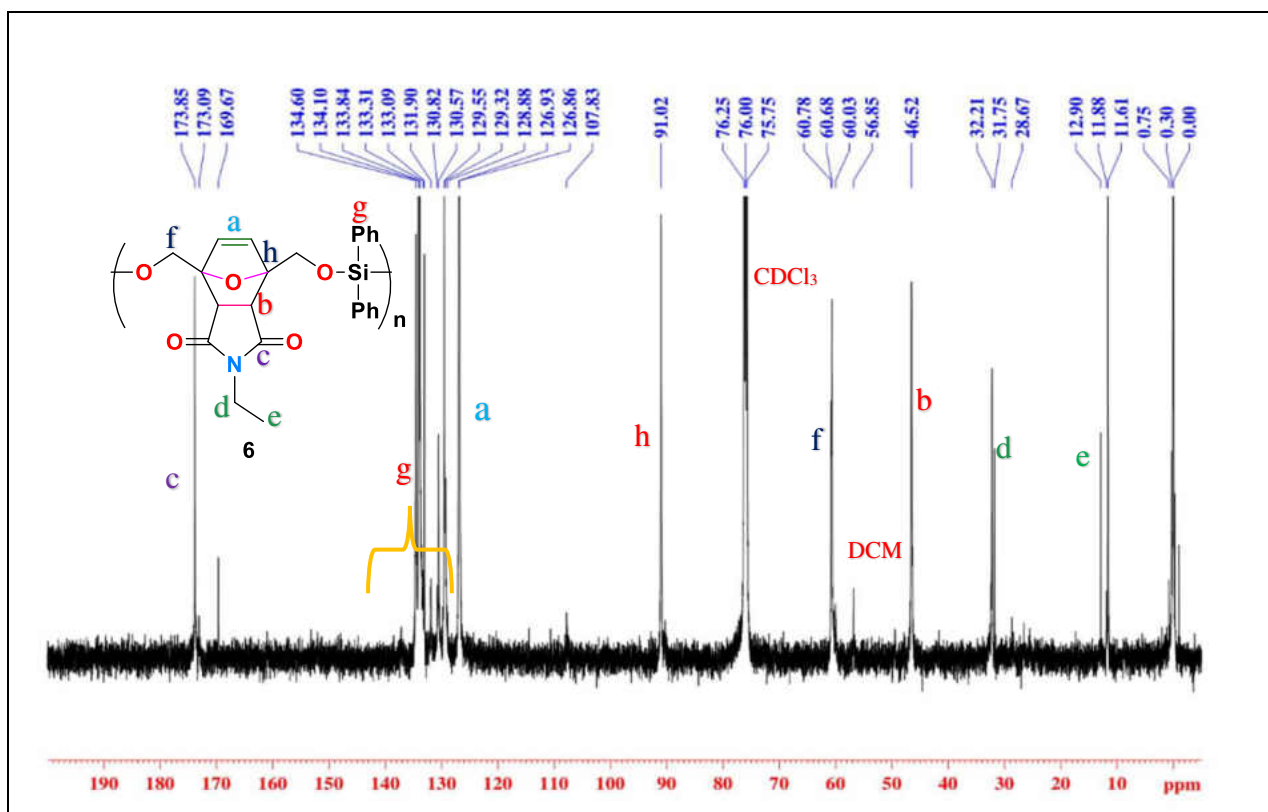
Figure 8. ^{13}C NMR of (PSEs/NEMI) DA-Adduct in CDCl$_3$.
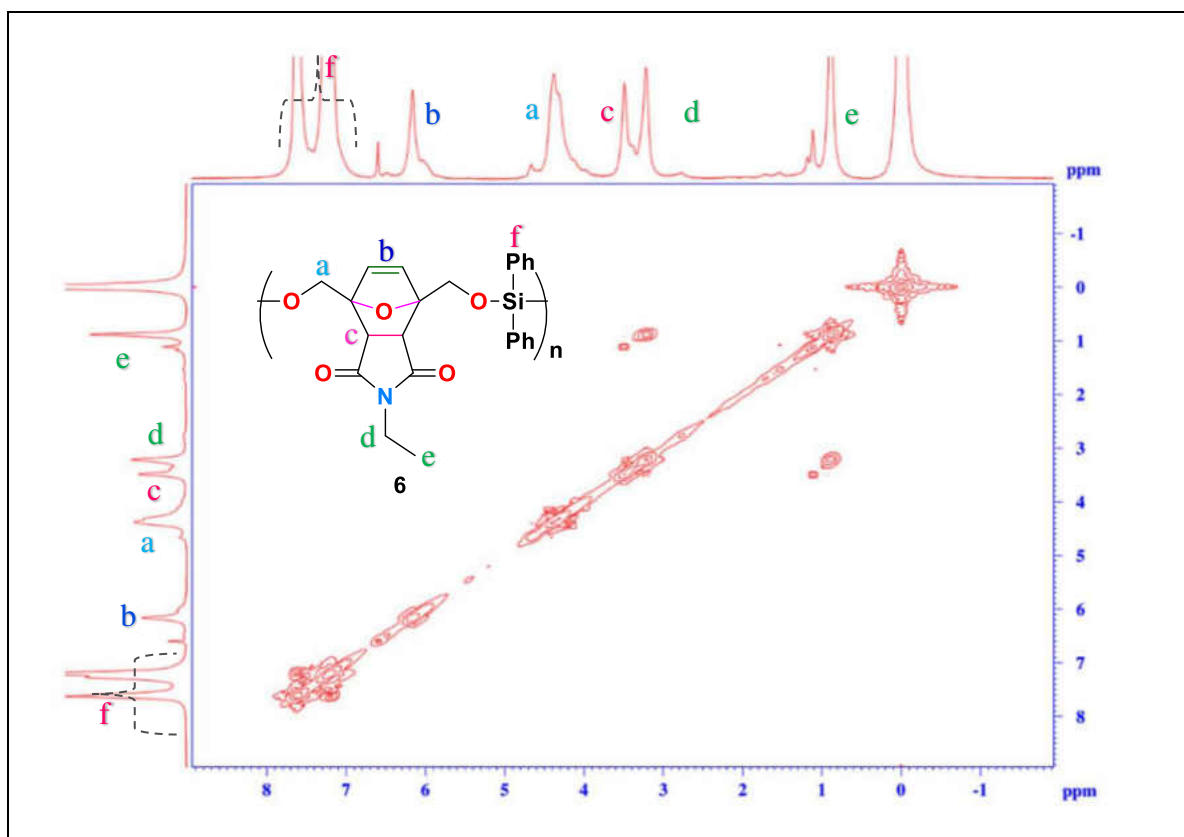
Figure 9. H-H correlation of DA adduct (**6**).

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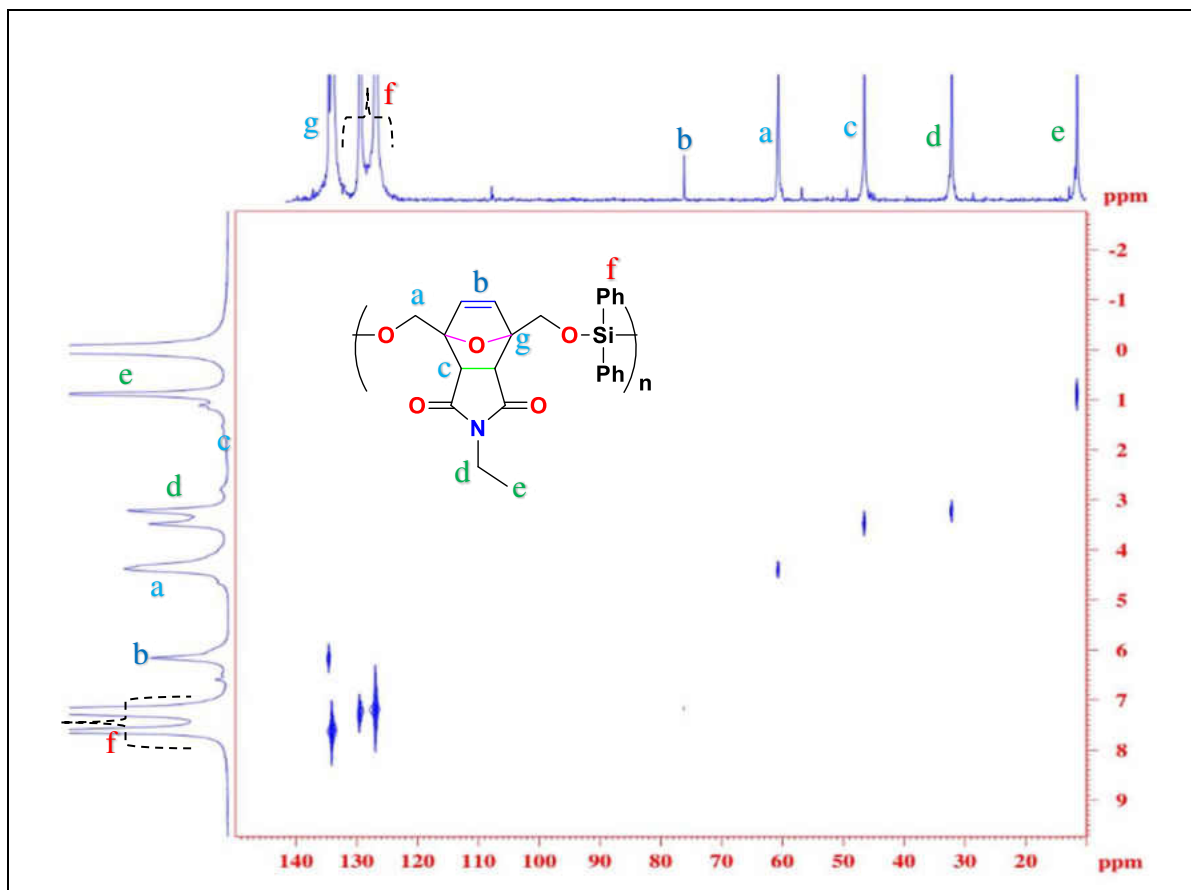
Figure 10. C-H correlation NMR of (**6**).
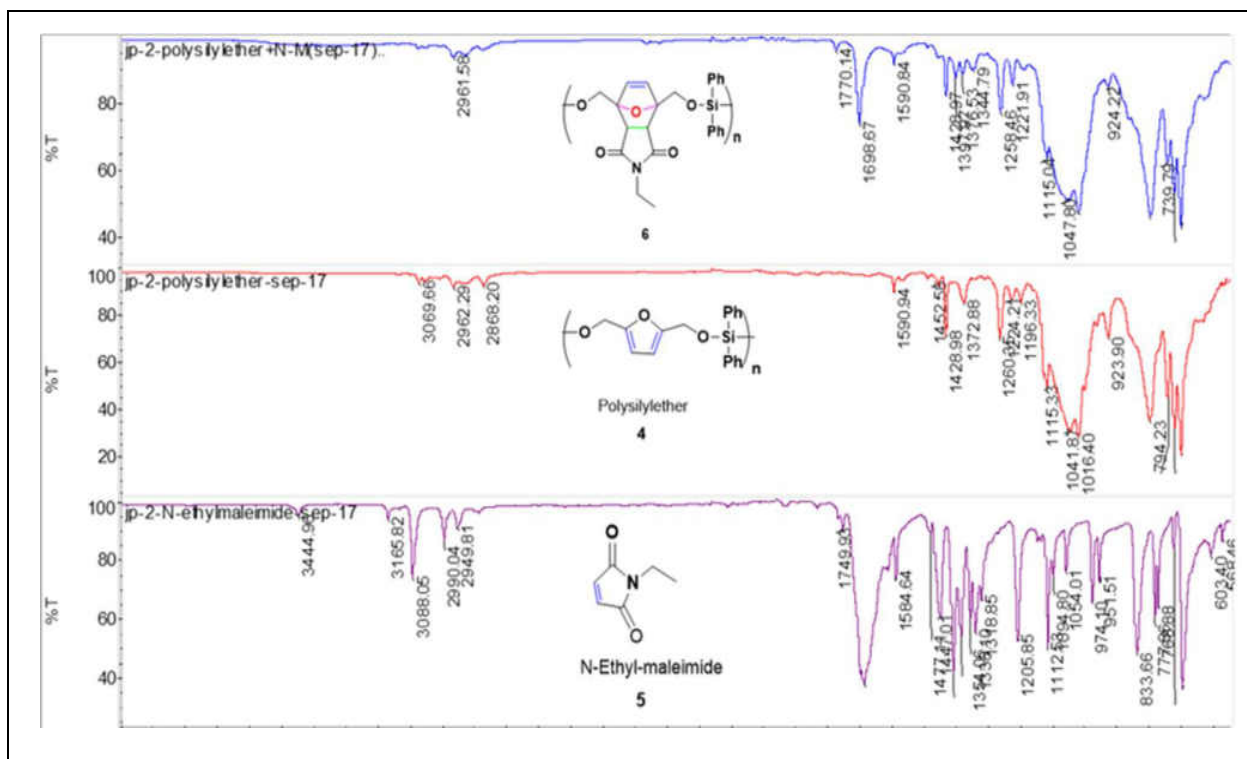
Figure 11. FT-IR Spectra of Reactant and Product.

2.3.2 Crossed-linked Polymer (7) (PSEBMI)

The crosslinked PSEs (**7**) were synthesized according to **Scheme 8**. Different ratios of Fu/Ma in the range of 1:0.25, 1:0.50, 1:0.75, 1:1, 1:1.25 and 1:1.5 were chosen to investigate the effect of the crosslinking density on the properties of the formed polymers. When the furan unit is in excess than maleimide, both ends of the crosslinking BMI will join into the network structure.[14] The appearance of the C=O stretching frequency at 1711 cm^{-1} and the Si−O−C linkage at 1260 cm^{-1} in the FT-IR spectra (**Figure 12**) supports the formation of the crosslinked polymer. The disappearance of the maleimide group's absorption peaks at around 829, and 689 cm^{-1} is the indication of the formation of crosslinked DA-adduct.
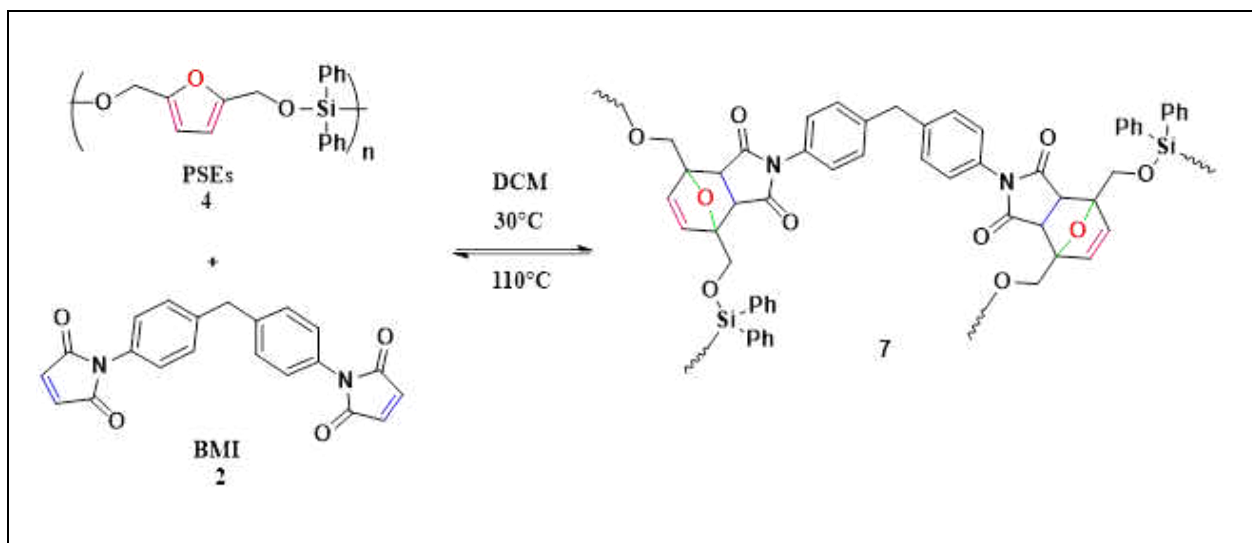
Scheme 8. Synthesis of Crosslinked PSEBMI DA-Adduct.
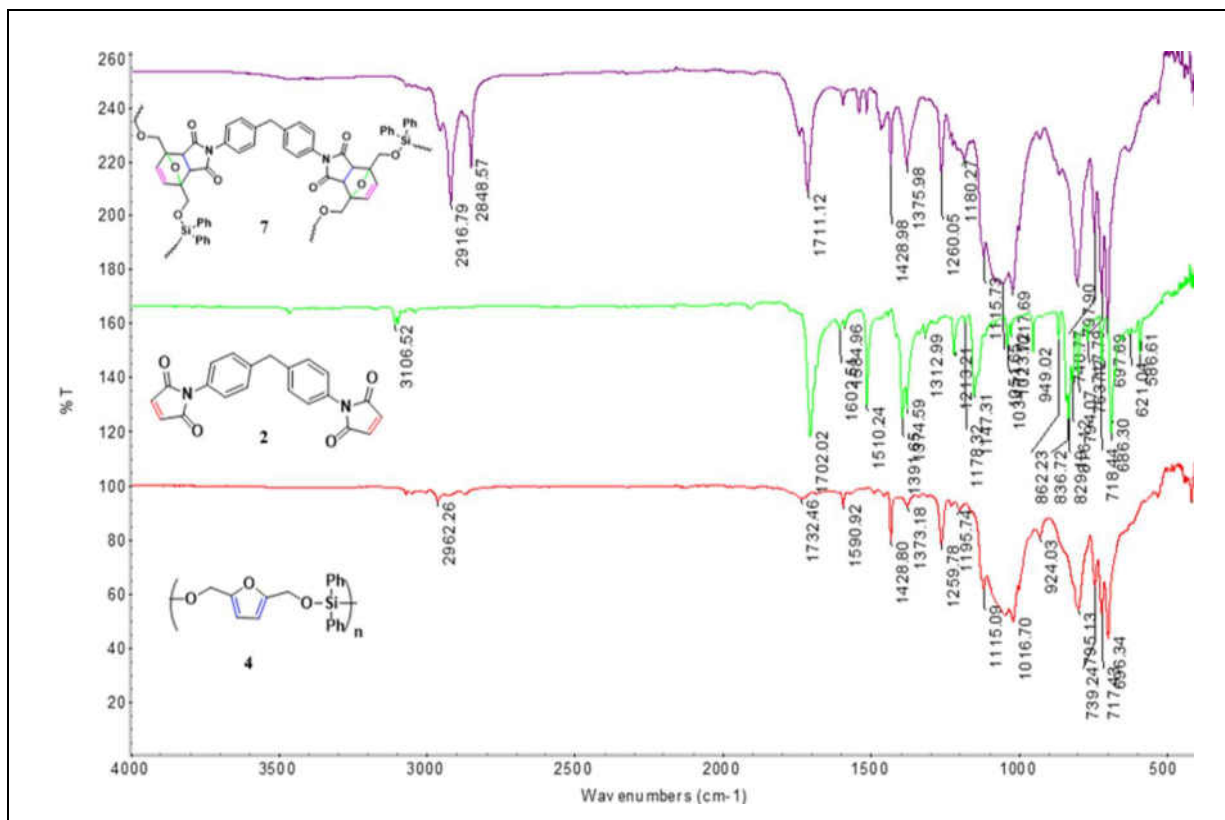
Figure 12. Comparison of Crosslinked DA-Adduct with Reactants by FT-IR Spectroscopy.
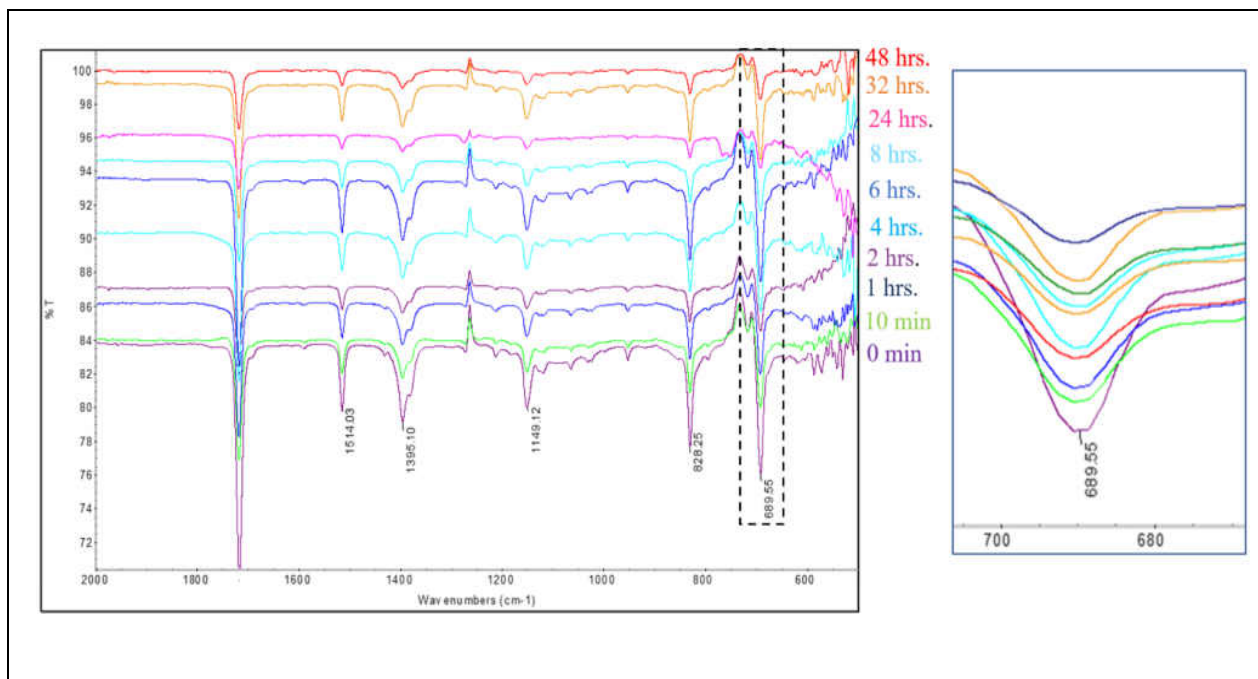
Figure 13. DA-Cycloaddition reaction Analysis of PSEBMI-1:1 at Different Time-intervals via IR Spectroscopy.

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The FT-IR spectroscopy also used to monitor the progress of the furan and maleimide Diels-Alder reaction at different time intervals. For this reaction, a mixture of PSEs and BMI (Fu/Ma ratio 1:1) dissolved in a 50 mL of DCM in a round bottom flask. The flask then put on a 40°C preheated oil bath for 48 h with constant stirring. As shown in **Figure 13**, the aromatic ring's absorption peak in the bismaleimide is in the region of 1510 cm^{-1}.[14,23.] It was used as a reference peak and remained unchanged during the reaction, while the maleimide (=CH) absorption peaked around 689 and 829 cm^{-1} diminished with time, comparable with the literature report.[14,23] This represents the DA- reaction progress with subsequent decrease of the maleimide peak.

2.4 Thermal Properties of Crosslinked Polymer (**7**)

2.4.1 Differential scanning calorimetry (DSC)

The differential scanning calorimetry (DSC) used to investigate the thermal behavior of the crosslinked **7** with different Fu/Ma ratios (**Figures 14 and 15**). The differences between the first and second heating cycles result from the reorientation of the polymer chain and the evaporation of the residual solvent or moisture content. Notably, two endothermic peaks are observed in both the first and second heating cycles in DSC thermograms of all the cases. These peaks range from 105 to 160 °C, corresponding to the r-DA. As discussed previously, the DA cycloaddition reaction gives two isomers, namely *endo*, and *exo*, which exhibit a broad range of the endothermic peaks upon heating. The *endo* adduct is the kinetic product, and it appears at a lower temperature compared to the thermodynamically stable *exo* adduct. [24-26]

At lower temperatures, around 105−135 °C, the less stable endo adduct undergoes r-DA reaction, while the *exo* adduct decomposes at higher temperatures around 150 °C and at prolonged reaction time. Another interesting observation is that when the furan/maleimide ratio varies from

1:0.25 to 1:1.5, the glass transition temperature increases (**Table 3**). PSEBMI-1:1.5 samples gave the highest glass transition temperature of 45 °C among all (**Table 3),** indicating that the stability and glass transition temperature increase as the crosslinking density increases.
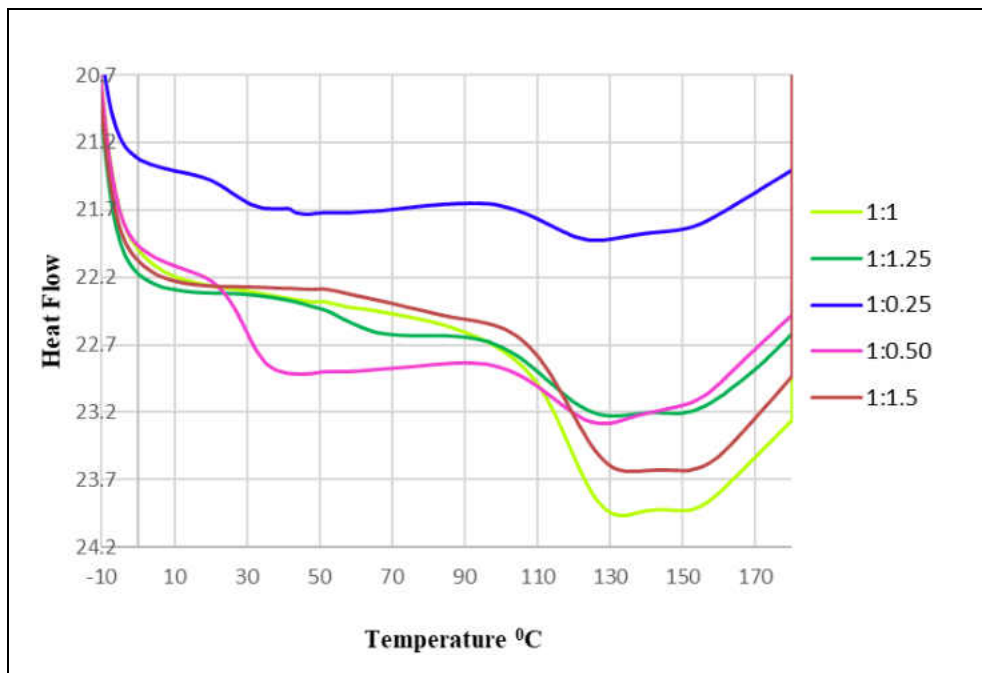
Figure 14. DSC curves of Different Adducts of Crosslinked PSEBMI. (2ⁿᵈ Cycle)
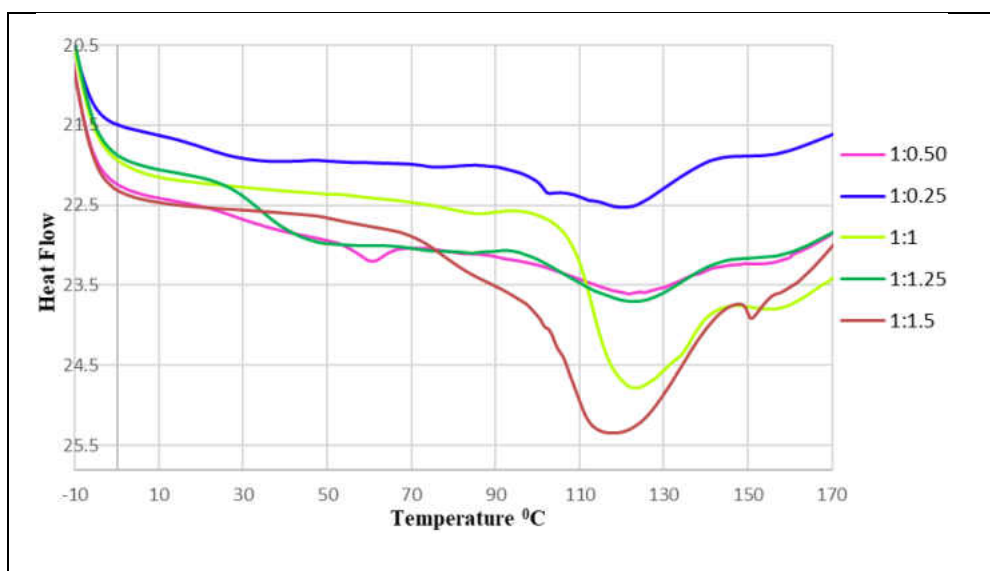
Figure 15. DSC Thermogram of (**7**) with Different Ratios of (**7**) (1ˢᵗ heating cycle).

2.4.2 Thermogravimetric analysis (TGA) of DA adducts
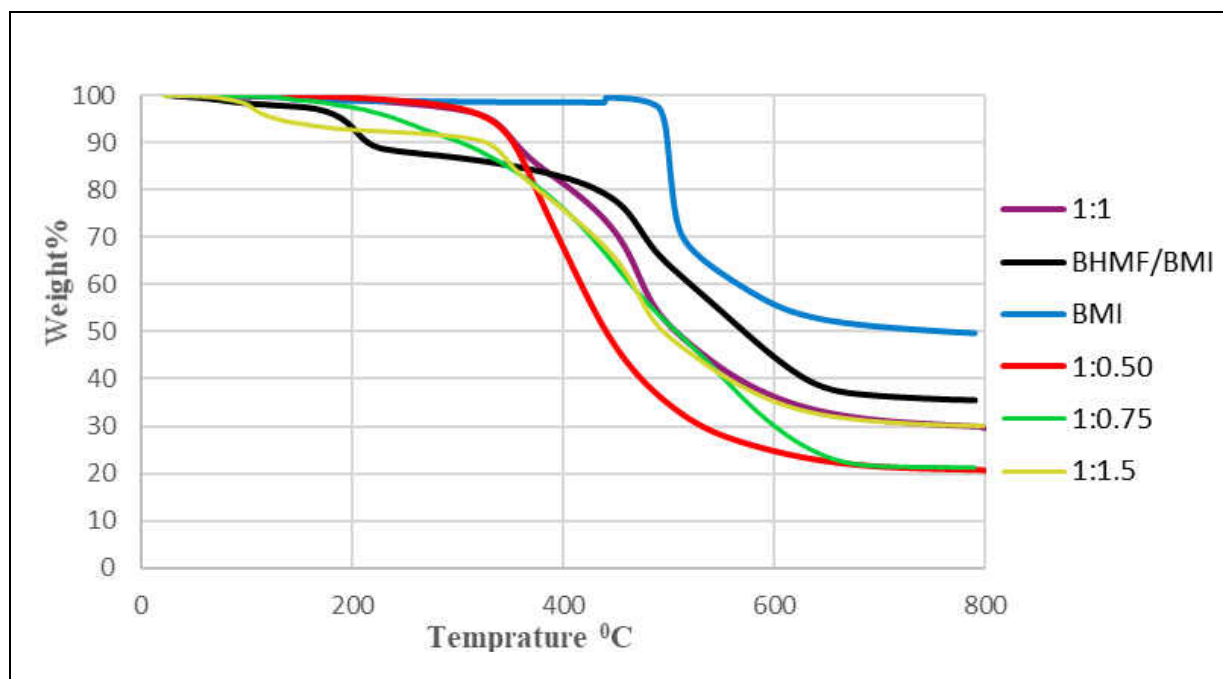
Figure 16. TGA Analysis of BMI, BHMF/BMI and Different $I_{ma/fur}$ Ratios.

The TGA analysis of (**2**), (**3**), and a series of (**7**) (samples with different ratios) are carried out in the temperature range of 200 to 800 °C (**Figure 16**). The temperatures at different weight losses are given in **Table 4**. The thermal behavior of the different samples of (**7**) is similar up to 120 °C, and the onset of decomposition is in the range of 124−235 °C. $T_{-50\%}$ (50% weight loss) occurs in between 440−508 °C. The final residue % of (**7**) is in the range of 20 to 30.0%. The PSEBMI-1:1.5 shows higher stability than PSEBMI-1:1, which is consistent with the DSC study. Tables 3 and 4 summarize the overall thermal observations from both DSC and TGA measurements.

Table 3. Thermal Analysis of various ratio of crosslinked PSEBMI from DSC.

DA Adduct	T_g/ °C	T_{rDA} (endo) °C	T_{rDA} (exo) °C
PSEBMI-1:0.25	17	119	152
PSEBMI-1:0.50	24	123	154
PSEBMI-1:1	26	124	153
PSEBMI-1:1.25	36	122	154
PSEBMI-1:1.5	45	122	151

Table 4. Comparison of Reactant and various crosslinked Samples by TGA.

Compound	T_g/°C	$T_{-1\%}$/°C	$T_{-5\%}$/°C	T_{-50}/°C	Final residue%	T_{max}/°C
PSEs	15.6	153	224	454	29	398
BMI	-	162	495	764	50	500
BHMF/BMI	-	74	190	572	35	474
PSEBMI-1:0.50	24	234	329	441	21	368
PSEBMI-1:0.75	-	146	241	507	21	449
PSEBMI-1:1	26	206	330	507	30	370
PSEBMI-1:1.5	45	85	129	495	30	444

2.5 Retro Diels-Alder Reaction

2.5.1 ^{1}H-NMR Analysis of r-DA of (**3**)

      To check the thermal reversibility of DA reaction in the current system, the DA adduct (**3**) heated at 110 °C, and the reaction monitored periodically by ^{1}H NMR (**Figure 17**). After 30 min, the characteristic 6.5 ppm signals of the double bonds −CH=CH− in the DA adduct (**3**) disappeared, and the new signals around 6.36 ppm and 4.45 ppm could be attributed to the starting materials (**1**) and (**2**). The *endo* and *exo* isomers peaks at 3.64, and 3.14 ppm, respectively, vanished from the spectrum. No further change was noted after 6 h. These observations indicated the DA reaction was readily reversible at 110 °C, and the starting materials could be recovered. It should also be mentioned that after cooling, the DA adduct re-formed within 24 h.
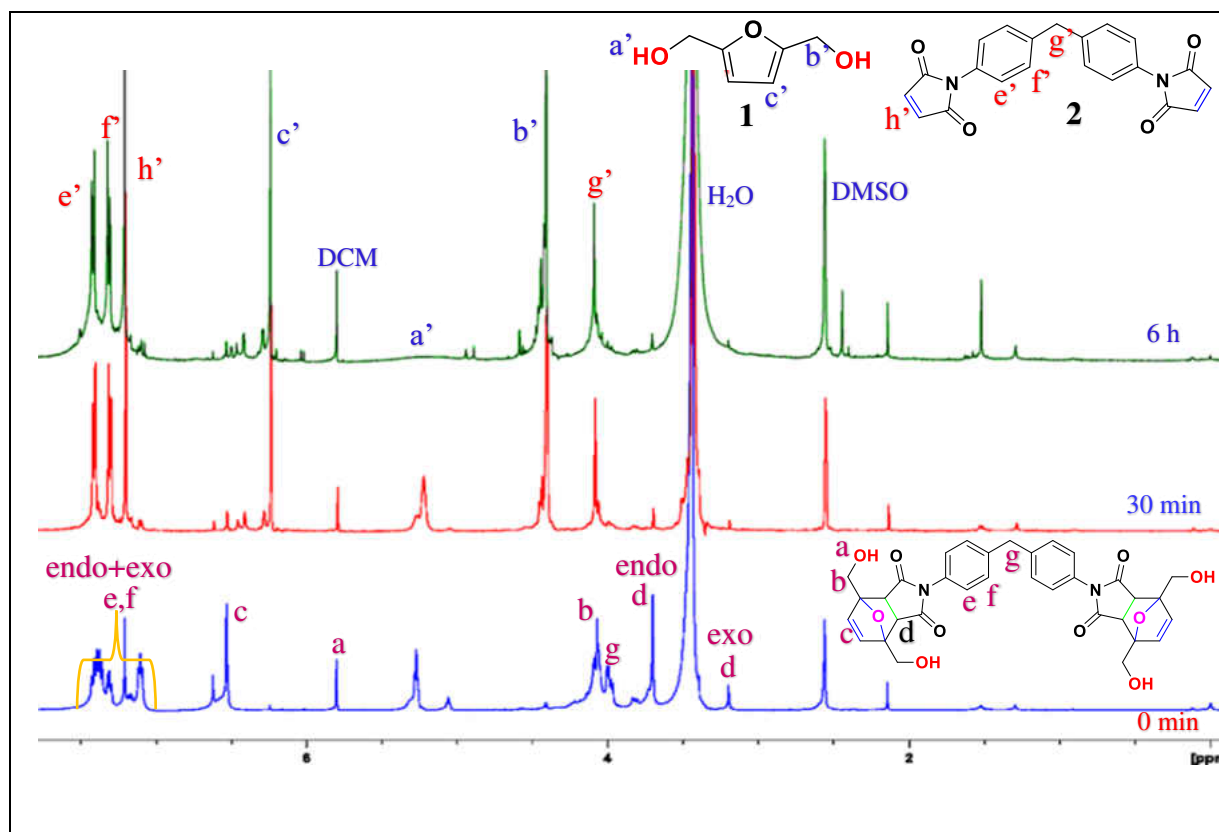
Figure 17. Retro-DA Reaction Analysis (Down is the Product and heating at 110 [0]C after 30 min. and 6 h.

2.5.2 Reversibility of the DA Adduct via Thermal analysis

Further evidence for the reversibility of the Diels-Alder reaction can be gleaned from the DSC experiments. The results in **Figure 14** and **15** show all the DA-adducts have broad endothermic peaks ranging from $105-154\,^0C$, which can be attributed to the retro DA reaction of the *endo* and *exo* isomers. Significantly, these peaks appear in both the first and second heating cycles, indicating that the DA reaction occurs again after the first heating cycle where the r-DA reaction takes place.

2.5.3 Reversibility and Recyclability Test for Crosslinked PSEs/BMI Specimen

The re-processability and reversibility of the crosslinked polymers were checked, as shown in **Figure 18**. The crosslinked specimen (PSEBMI-1:1.5) was cut into the small pieces (a). These pieces were placed in a vial (b) and heated at 110 °C. The reversible reaction and decrosslinking occurred at a higher temperature. It melted in a few minutes (c). When it cooled down slowly, the DA-reaction formed a network structure again. The obvious observation here is the re-crosslinking (d). Remolding of this material again re-forms a PSEBMI specimen (e).[27,28]
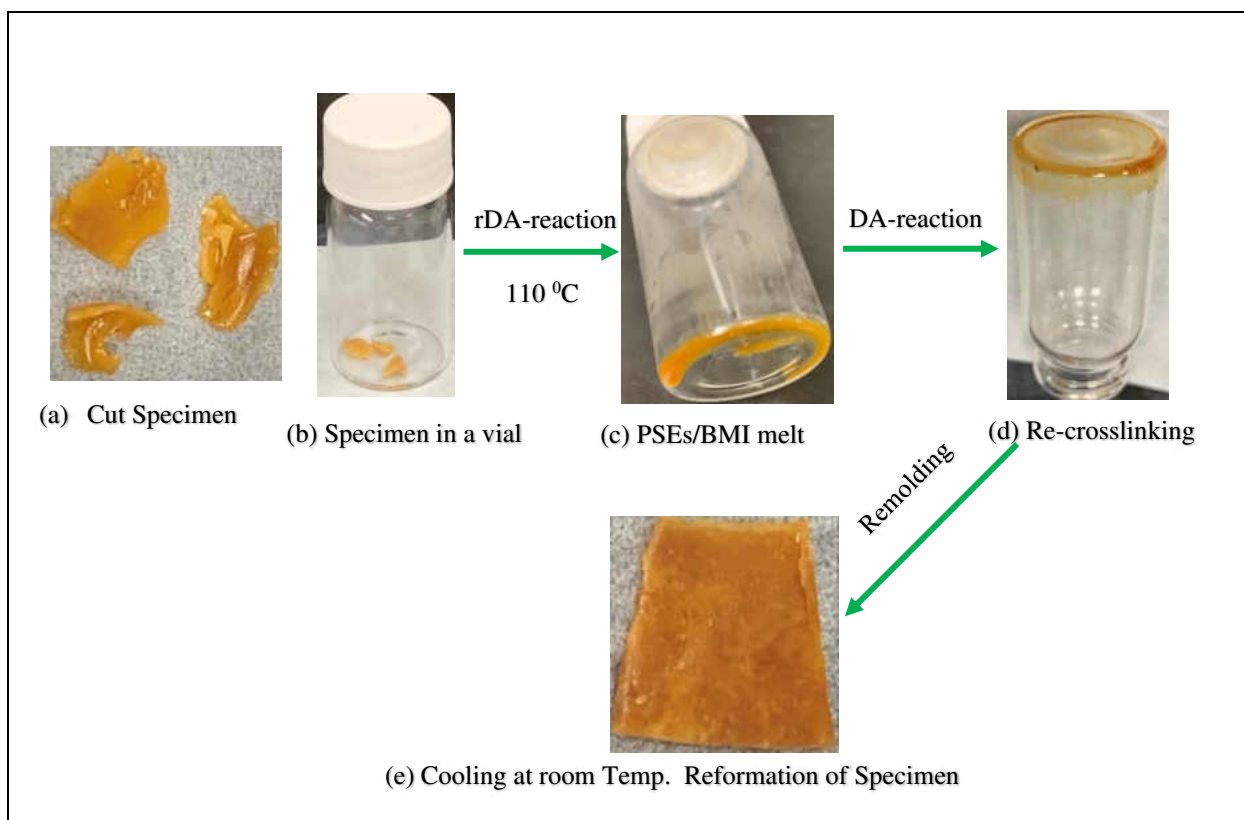
Figure 18. Photographs taken to represent the Reversibility and Re-processability Analysis of Crosslinked Sample.

2.6 Self-healing of crosslinked PSEBMI Film

The basic requirements for self-healing are (a) accessibility and sufficiency of reactive functionalized groups. A higher concentration of these moieties helps speed up the chemical kinetics. It can also provide the active sides for the reaction to heal the damage; (b) mobility of the polymer chain is another necessity for filling the crack or damage in self-healing; (c) sufficient contact time are also required to allow reaction of free functional groups for sealing the crack or cut in damaged surfaces.[29]

There are different methods to achieve self-healing. The most widely used self-healing technique is thermal self-healing, in which polymer is heated above the temperature of its glass transition (T_g).[30] Another is room-temperature healing, demonstrated by the mere application of

pressure. To evaluate the self-healing properties of crosslinked polymers **7**, we used two different methods.

2.6.1   Room Temperature Pressure-Assisted Self-Healing

To demonstrate quick self-healing, we scratched the surface of PSEBMI-1:0.75￼ with a razor in the middle (**Figure 19**). After a few minutes, it was observed to heal, as shown in the photo images. After 24 h. it almost healed. After 30 days, even a deep scratch at the corner of the sample disappeared. That's the success of the self-healing. Likewise, one piece of PSEBMI-1:0.75 (**Figure 20**) was cut into two parts with a razor.￼ By applying gentle hand pressure from both ends for a few minutes and then used the laboratory clamps to put pressure on both the parts of the cut sample, the two regions started to join back together. These behaviors are the indication of the immediate reestablishment of the crosslinking polymer network.[31,32] The flexibility of the Si−O bond may provide enough mobility to facilitate the binding.[33]￼ However, a complete recovery was not reached.
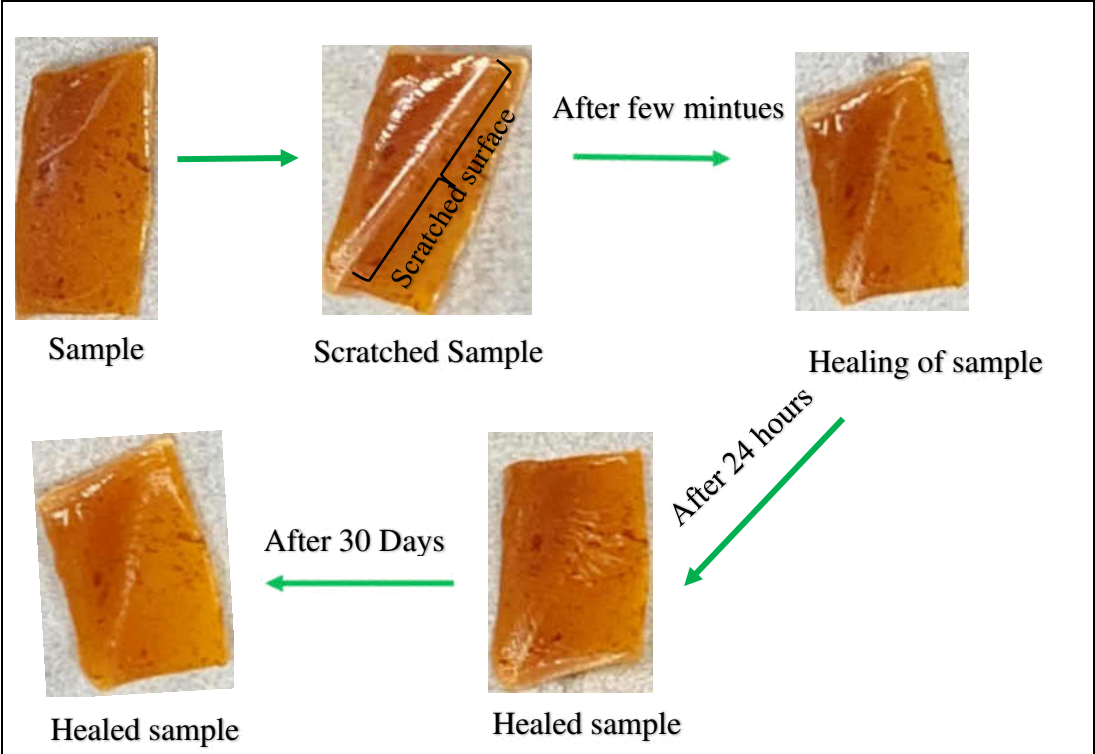
Figure 19. Pressure Assisted self-Healing test of Scratch Specimen. (Photo Images)
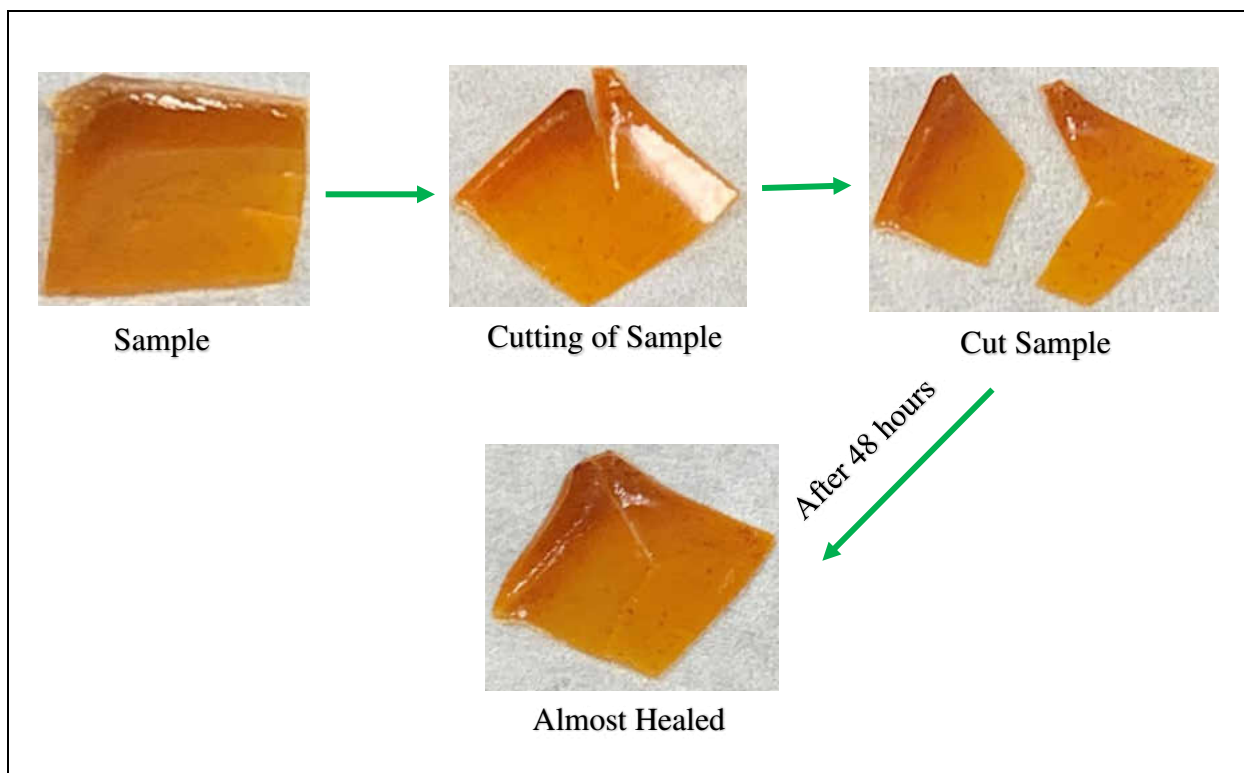
Figure 20. Self-Healing Test of Cut Sample via pressure. (Photographic Images)

2.6.2 Solvent Assisted Healing of Crosslinked Film

A proper solvent may facilitate another pathway for rapid self-healing by implementing enough mobility into the network, so unreacted maleimide and furan moieties may easily reconnect by the DA-reaction. Two drops of the solvent DCM were added to see the effect of the solvent assisted self-healing in both cut and scratched surfaces in the same sample (PSEBMI-1:0.75). As shown in **Figure 21,** both the scratched and cut surfaces started to recover. After two days, the surfaces almost completely healed.
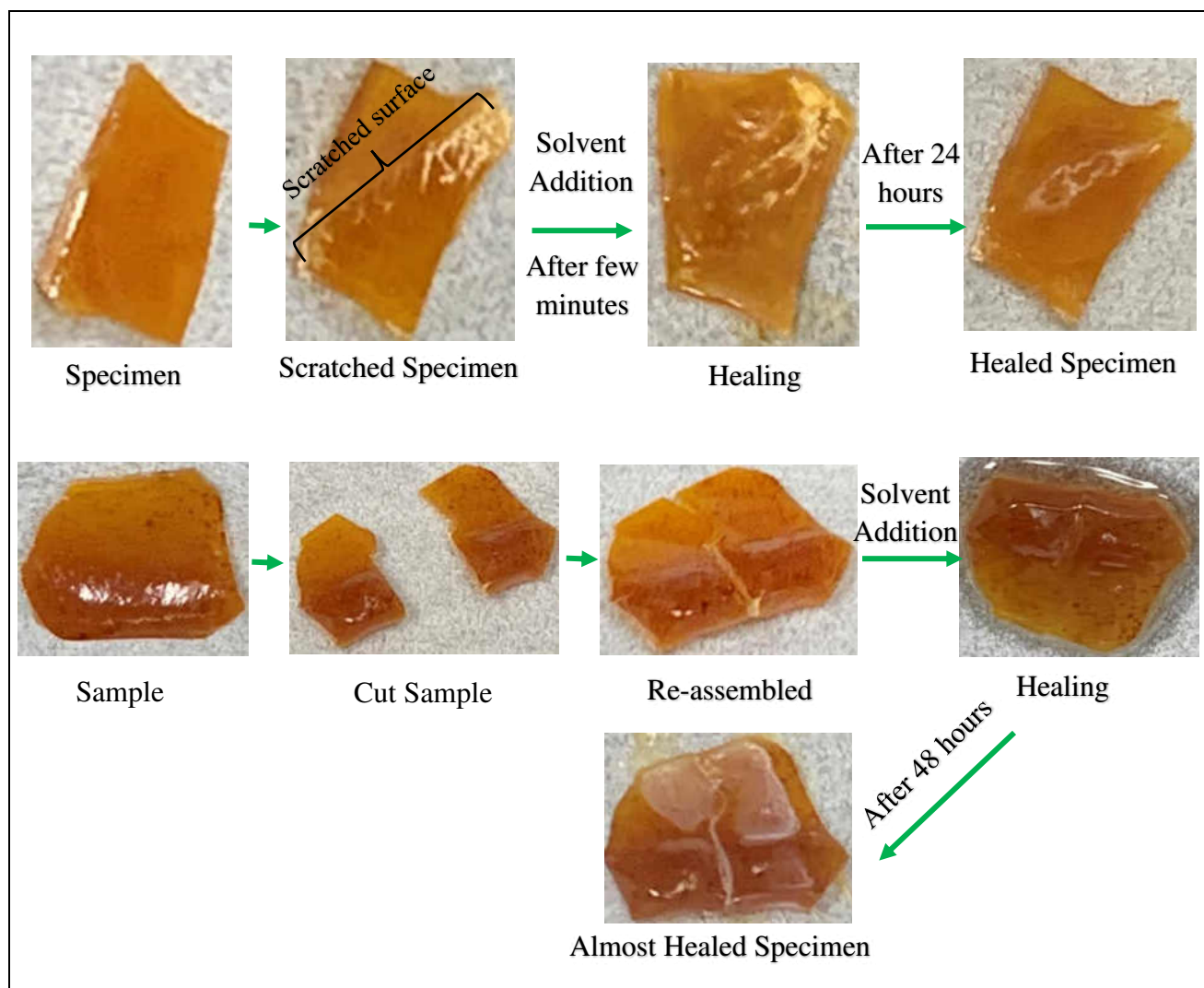
Figure 21. Photographic images of Solvent Assisted Self-Healing on Scratch and Cut Samples.

2.7 Degradation Analysis of Crosslinked Product (**7**)

The degradability of the crosslinked polymers (**7**) was studied by acidic hydrolysis. The general procedure explanation is given by sample (**7**) is as follows, a suspension prepared by suspending the fine powder of sample (**7**) with Fu/Ma ratio of 1:0.15) in THF (~ 10 mg/mL). An equal portion of the HCl/H_2O (pH ~ 2) solution added, and the mixture was stirred for 48 hours. [11] Characterization by ^{1}H-NMR (**Figure 22**) shows the generation of the DA adduct **3** expected for the hydrolysis for the silyl ether linkages, as indicated by the peaks at 6.5 ppm.
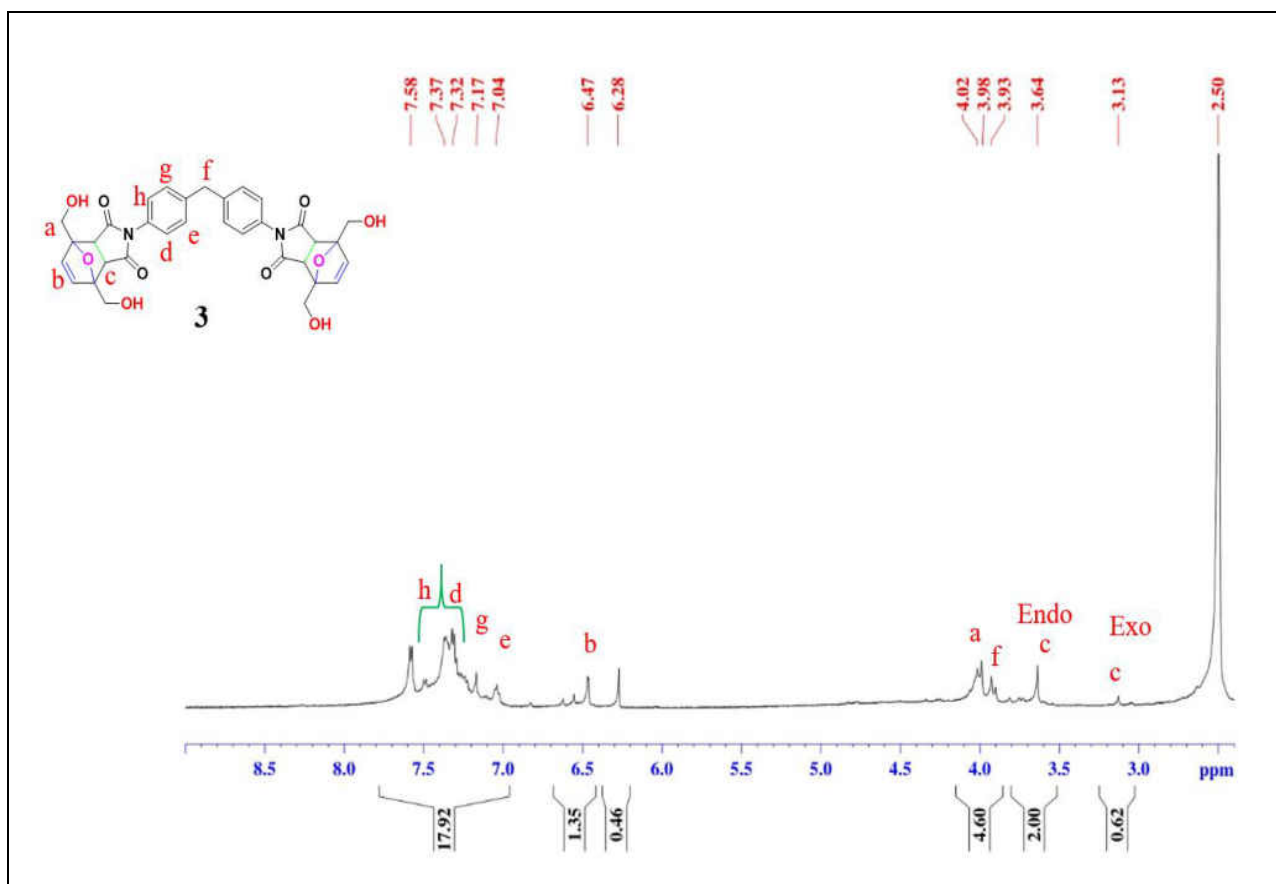
Figure 22. ^{1}H NMR of hydrolyzed product of DA-adduct (**7**).

CONCLUSIONS

Our study has demonstrated that the Diels-Alder reaction between furan and maleimide could be employed in modification and crosslinking of the furan derived poly(silyl ether)s. Different amounts of bismaleimide agents are used to construct the crosslinked polymer network with different crosslinking density. The crosslinking process can be monitored at different time intervals by FTIR spectroscopy. NMR and DSC analysis confirm the reversibility of the DA reaction. The strong endothermic peaks in the range of 105−154 °C in DSC thermograms represent the rDA reaction. The higher thermal stability and higher T_g were also observed in 1:1.5 PSEBMI, in the DSC analysis among all the ratios of crosslinked polymers, which indicates that the crosslinking density increases stability and glass transition temperature. The healing of scratched

and cut samples exhibit good room-temperature and solvent assisted self-healing efficiency. Also, the network polymer shows excellent recyclability and reversibility. Ideally, the dynamic mechanical analysis and other quantitative measurements will be needed for more detailed study. These findings show that PSEs crosslinked with dynamic bonds help to impart reprocessibity and self-healing properties into the material, which makes them an intriguing subject for further research.

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