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Reversible releasing of arms from star morphology polymers

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ABSTRACT

Reversible thermally induced arm release from a star polymer morphology was prepared which consists of furanic functional core and maleimide functional arm which are attached or detached via Diels–Alder (DA) reversible reactions. This approach allows the reversible bonding and debonding at 35–40 °C (DA) and 90–100 °C (retro-DA). The covalent reversibility of this process consists of 7 cycles of the DA and retro-DA reactions.

The major advantage of designing and developing polymers capable of responding to stimuli comes from their ability to change physical and/or chemical properties as well as their architectures in a controllable and predictable fashion. Thermal responsiveness has drawn significant attention and a majority of studies focused on transformations involving non-covalent interactions leading to swollen or unswollen states in response to temperature or pH changes [1–5]. However, incorporation of reversible covalent bonds into a polymer structure is significantly more challenging, but highly rewarding as it may lead to higher chemical stability while retaining the possibility for cleavage, reformation, and/or reorganization. Polymer structures with a reversible covalent linkage will enable the design of switching between simple and more complex architectures. Examples of reversible covalent reactions include thermo-reversible Diels–Alder chemistry [6–15], photo-reversible olefin cyclo-additions [16], thiol driven reversible sulfide coupling [17], pH driven boronic–salicylic hydroxamic acid coupling [18], and thermally cleavable alkoxyamines [19].

Thermally reversible DA reactions have been utilized in numerous studies including polymer synthesis [8,11,15,20–22], surface modifications [23,24], organic–inorganic polymer hybrids [12,25], reversible crosslinking polymer chains/gels [6,7,9,12–14,23], and remendable/self-healing polymers [26]. Due to the fact that these reactions can proceed under mild conditions without a catalyst, thus makes them attractive for designing covalently reversible bonds in which furan and maleimide functional groups are responsible for association and disassociation [24,26,27]. In this study, we took advantagable of these conditions and report the formation of star polymers with reversibly removable arms, which was accomplished by Diels–Alder (DA) [4 + 2] cyclo-adduct, where the arms were attached and detached in response to thermal stimuli. Although there are a number of reported examples [27–29] of thermally reversible cleavage using Diels–Alders reactions, to our best knowledge this is the first study that shows fully reversible covalent bonding and debonding of arms from a star-like polymers architectures. Scheme 1A illustrates the overall diagram of this process and reversible chemical reactions are illustrated in (B).

Thermally reversible star polymer preparation involves synthesis of the star core with furan end-groups and star arms with maleimide functional groups. The star core with the furan end-groups was synthesized by reacting 1,1,1-tris(aminomethyl) ethane (Sigma–Aldrich Co.) with furfuryl isocyanate (Sigma–Aldrich Co.) at the 1:3 stoichiometric ratio as shown in Scheme 2. ATR-FTIR spectra in Fig. 1 illustrate the formation of the furanic star core which is manifested by the presence of the bands at 1650 cm^{-1} and 1550 cm^{-1} due to the C=O and N–H vibrations of the urea linkage and the 1516 cm^{-1} band due to furan double bonds, respectively [30]. The star arm used in this study was *N*-butylmaleimide (Sigma–Aldrich Co.) with the bands at 1662 cm^{-1} and 1150 cm^{-1} due to the maleimide double bond and C–N–C linkage, respectively [30]. ^{1}H NMR spectra shown in Fig. 2 illustrate that the methylene proton of 1,1,1-tris(aminomethyl) ethane shifts from 4.5 ppm to 4.2 ppm and the methylene proton of furfuryl isocyanate shifts from 2.3 ppm to 2.8 ppm, thus indicating the formation of the urea linkage of the star core [30]. The choice of *N*-butylmaleimide was dictated by the easy of analyzing low molecular weight model that may serve for further studies for controllable arm release polymers.

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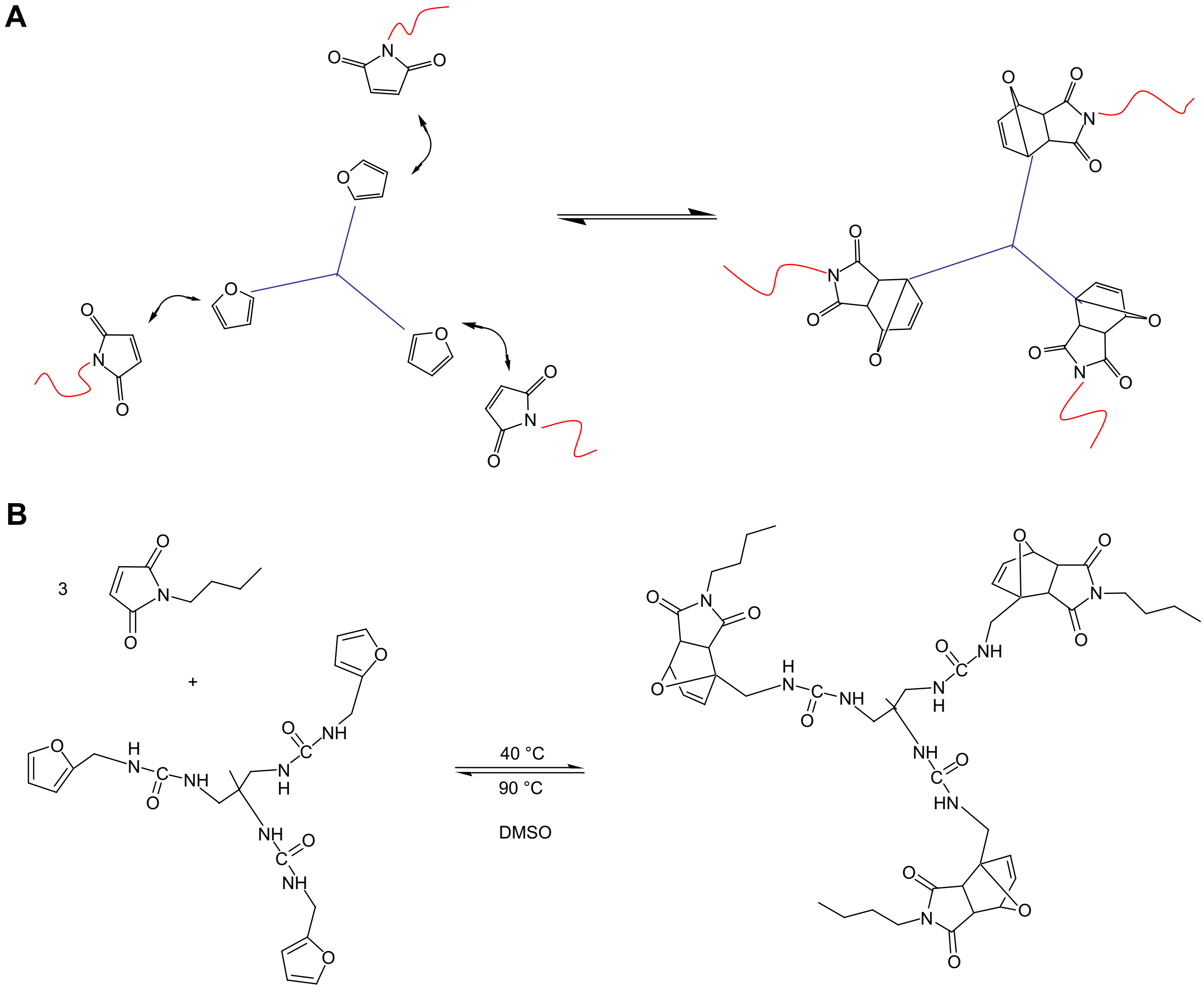
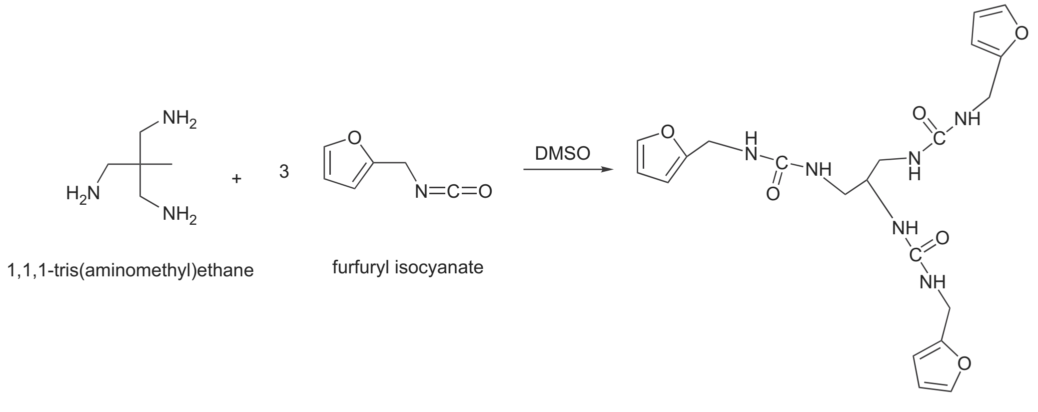


Scheme 1. (A) The model representation of the fully reversible covalent bonding and debonding arms. (B) Chemical reaction of the reversible maleimide arms' removal and attachment to the furanic star core.

The reversibility of the star formation via DA reactions shown in Scheme 1 was monitored using ATR-FTIR and ^{1}H NMR spectroscopies and forward–reverse bonding–debonding was conducted at 35–40 and 90 °C, respectively. ATR-FTIR spectra illustrated in Fig. 3 show the disappearance of the key bands at 1662 cm^{-1} and 1530 cm^{-1} due to maleimide and furan double bonds, respectively [30], and vanish at 40 °C to reappear again at 100 °C. Similarly, ^{1}H NMR spectrum at 40 °C in Fig. 4 shows a resonance at 5.2 ppm due to the bridge-head CH proton of the DA adduct [23,24,30], which disappears at 90 °C and reappears again at 40 °C, this showing again the reversibility of the arm attachment. In an effort to establish the lifetime of reversibility the reaction shown in Scheme



Scheme 2. Reactions of 1,1,1-tris(aminomethyl) ethane and furfuryl isocyanate leading to furanic star core formation.

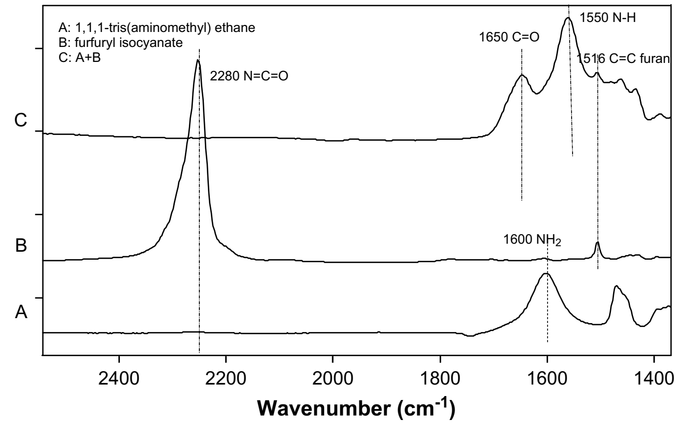


Fig. 1. ATR-FTIR of the star core formation.

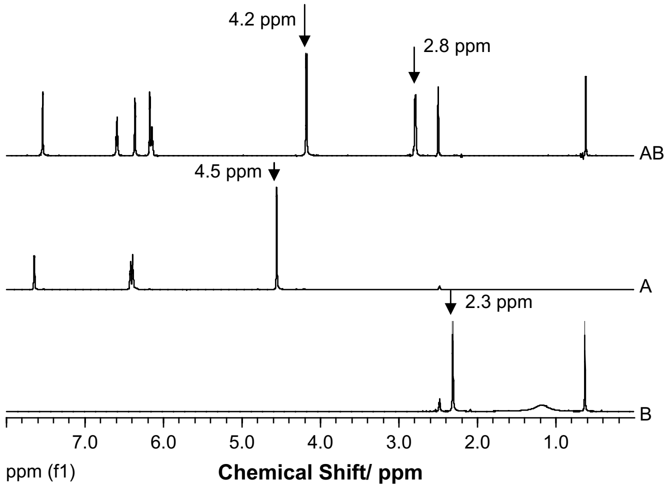


Fig. 2. ^{1}H NMR spectra of furanic star core; A: furfuryl isocyanate, B: 1,1,1-tris(aminomethyl)ethane, AB: furanic star core formation.

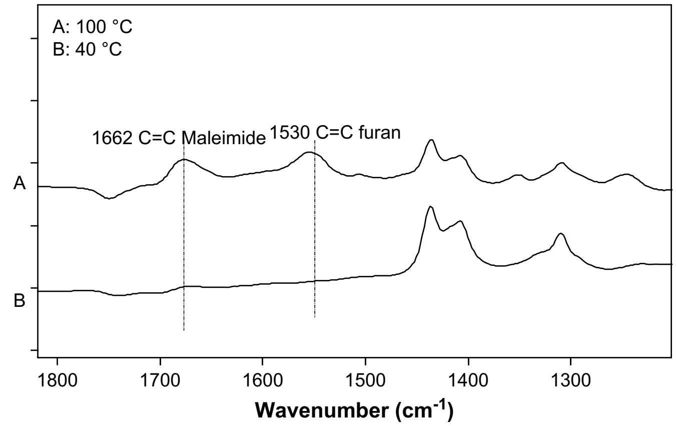


Fig. 3. ATR-FTIR spectra of reversible star polymer in response to thermal stimuli.

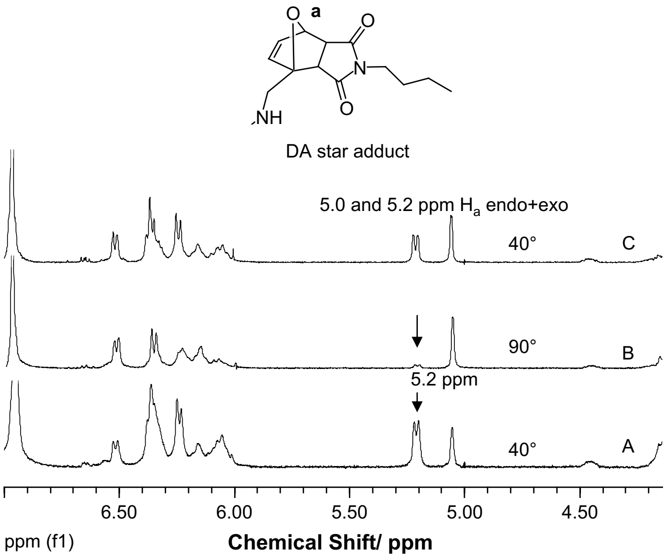


Fig. 4. ^{1}H NMR of the DA adduct formation recorded at; A: reaction mixture at 40 °C; B: reaction mixture was heated to 90 °C; C: reaction mixture was cooled to 40 °C.

2 was conducted back and forth several times and the covalent reversibility of this process lasted up to 7 cycles of the DA and retro-DA reactions.

In order to determine the efficiency of the arm release and attachment after each cycle, an average molecular weight of the core-arm assembly was calculated using ^{1}H NMR data. The integrated area of 7.5 ppm resonance due to the protons of the unreacted furan ring was ratioed against the resonance at 5.0 and 5.2 due to the proton of the adduct bridge. Using this approach the reaction yield efficiency f_{adduct} was calculated and normalized to 100%. While the theoretical average molecular weight of the star polymer is $M_{\text{star}} = M_{\text{core}} + 3(M_{\text{arm}} \times f_{\text{adduct}})$, where M_{star}, M_{core}, and M_{arm} are the molecular weights of each component and f_{adduct} is the yield efficiency (for $f_{\text{adduct}} = 1$, a 100% yield is anticipated), using ^{1}H NMR data the experimentally determined f_{adduct} value after the first cycle was 0.95 which corresponds to $M_{\text{star}} = 923$ g/mol. After the 7 cycles, the f_{adduct} of the furan that formed the adduct decreased to 0.76, which is likely to the volatilization of the maleimide arms and the average molecular weight of the star polymer was 831 g/mol.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2008.10.048.

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