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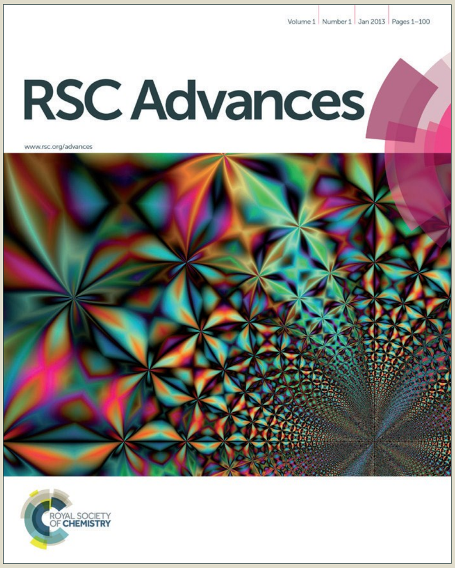

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A minimalist furan-maleimide AB-type monomer and its thermally reversible Diels-Alder polymerization

Talita M. Lacerda,[a,b,c] *Antonio J. F. Carvalho,*[c] *Alessandro Gandini*[b,c*]

[a] Biotechnology Department, Engineering School of Lorena, University of São Paulo,
Estrada Municipal do Campinho, s/nº, 12602-810 Lorena, SP, Brazil.
[b] São Carlos Institute of Chemistry, University of São Paulo, Avenida Trabalhador
São-carlense 400, 13566-590 São Carlos, SP, Brazil.
[c] Department of Materials Engineering, São Carlos School of Engineering, University
of São Paulo, Avenida João Dagnone 1100, 13563-120 São Carlos, SP, Brazil.

The present study reports an easy and direct route for the synthesis of highly pure 2-furfurylmaleimide, a minimalist furan-maleimide AB-type monomer, which was used for the preparation of a rigid thermally reversible polymer based on the Diels-Alder reaction. This strategy has a high potential for the development of novel polymers and copolymers mainly derived from renewable resources.

The versatile Diels-Alder (DA) click reaction of the furan (diene)-maleimide (dienophile) pair is a well-defined tool in organic synthesis and has recently gained much attention in the field of polymer synthesis and modification, offering a green connotation by combining furan compounds as renewable resources with clean and straightforward processes.[1] Additionally, based on its thermal reversibility (**Scheme 1**), this reaction opens the way to the preparation of self-mendable and recyclable

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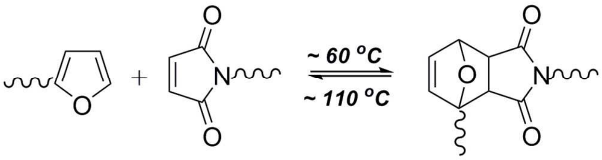
macromolecular materials possessing a variety of architectures, thus enhancing their potential applications, as recently reviewed,[1] with updates[2] and extension to biomaterials.[3]



Scheme 1. The furan-maleimide DA equilibrium illustrating a thermally reversible polycondensation step (the *endo* and *exo* structures of the adduct are not shown).[1]

We describe here a peculiar synthesis and polymerization of a highly pure AB-type monomer containing a single methylene moiety bridging the furan heterocycle with the maleimide counterpart, viz. 2-furfuryl-*N*-maleimide (**5, Scheme 2**), for the preparation of a rigid, thermally reversible linear polymer based on the DA/retro-DA (rDA) reactions based on Scheme 1. A previous study[4] had tackled this topic, but with unsatisfactory results because of the inadequate approach to the monomer synthesis, which gave rise to poor polymerization processes. We decided therefore to tackle the issue through a different approach that involved the in situ synthesis of the corresponding polymer **4** (Scheme 2) to be used as a precursor to the monomer **5** by calling upon its rDA depolymerisation. Scheme 2 highlights this strategy.

The procedure consisted initially in carrying out the 1:1 reaction of 2-furfurylamine (**1**) and the previously synthesized classical furan-maleic anhydride DA adduct (exo-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride, **2**), conducted in methanol at 55-60 °C for 3 days, to prepare the protected analogue (ProtAB, **3**) of the AB monomer **5**, which was characterized by FTIR and ^{1}H NMR spectroscopy. Its deprotection, a simple rDA reaction for the elimination of furan, was conducted in

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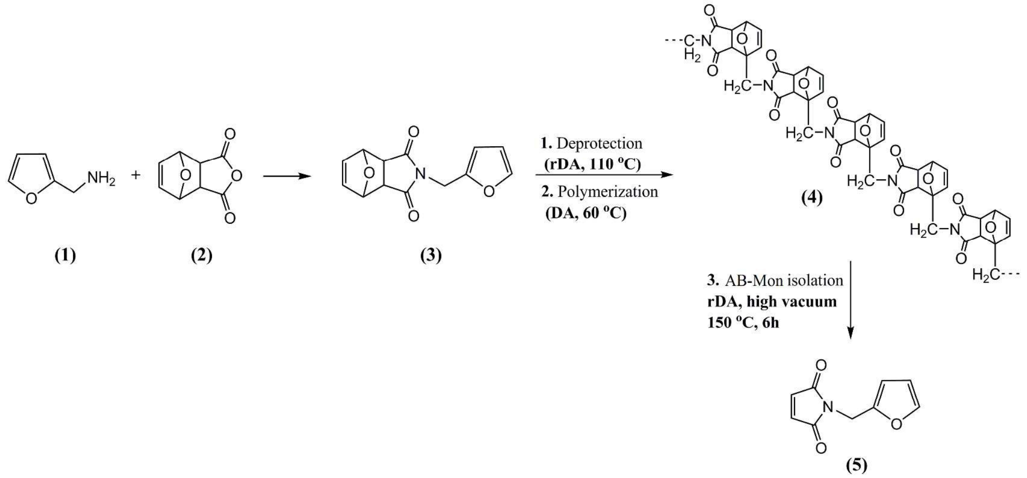
1,1,2,2-tetrachloroethane (TCE) at 110 °C for 5h. Once the release of the protecting furan had been completed, leaving a maleimide group susceptible to undergo the DA reaction with the complementary furan moiety at the other end on this very short AB structure **5**, the temperature of the system was decreased to 60 °C, which shifted the DA equilibrium towards the formation of the adduct (Scheme 1) and hence promoted the monomer polycondensation giving both *endo* and *exo* stereoisomer units in the backbone.[1] The ensuing polymer (PolyAB, **4**) was characterized by FTIR and ^{1}H NMR spectroscopy and thermal analyses. GPC could not be carried out because the polymer was not soluble in the organic solvents commonly used with this technique, which might be a consequence of its inherent rigid structure. In the final key step, the desired AB monomer **5** was generated by heating polymer **4** at 150 °C for 6 h in a high-vacuum flask equipped with a liquid nitrogen cold finger. Its rDA depolymerization reaction released the AB monomer, which was collected on the cold finger as high-purity white crystals and whose structure was confirmed by FTIR and ^{1}H NMR spectroscopy. The thermal properties of the monomer were also evaluated.



Scheme 2. Schematic route for the isolation of pure 2-furfuryl-*N*-maleimide and its DA polymerization.

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Figure 1 shows the FTIR spectra of **3**, **4** and **5** in which the most relevant discriminating features are the differences around 1000 cm^{-1}, related to the presence (**3** and **5**) and absence (**4**) of the typical furan breathing peak, and around 840 cm^{-1}, related to the presence (**5**) and absence (**3** and **4**) of the characteristic maleimide peak. **Figure 2** displays their respective ^{1}H NMR counterparts with the corresponding assignments. In the case of polymer **4** spectrum, the presence of both *endo* and *exo* adducts gave rise to broader resonance features.

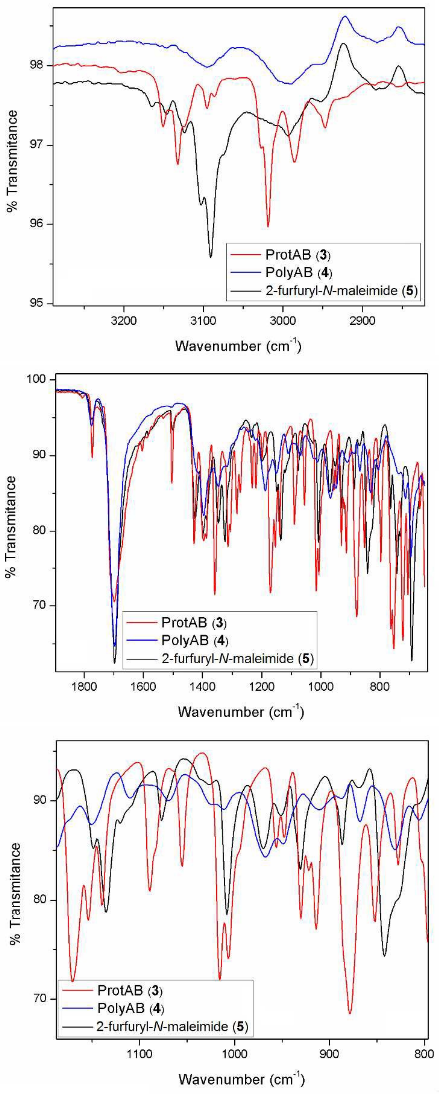

Figure 1. FTIR spectra of ProtAB (**3**), PolyAB (**4**) and 2-furfuryl-*N*-maleimide (**5**), highlighting different wavenumber regions.

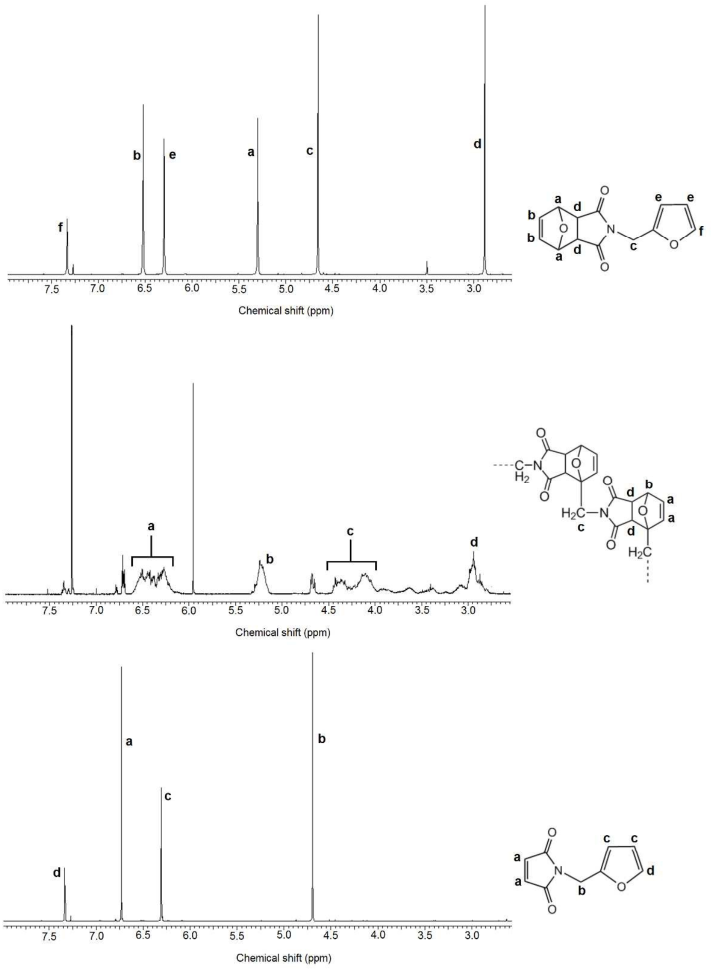

Figure 2. ^{1}H NMR spectra of ProtAB (**3**), PolyAB (**4**) and 2-furfuryl-*N*-maleimide (**5**).

The thermogravimetric analysis of polymer **4**, performed under a nitrogen atmosphere, showed an initial degradation at 110 °C with a more prominent weight loss from 150 °C, with only 10% of residue left at 230 °C (**Figure 3A**). This behaviour was in tune with a depolymerisation process induced by the rDA reaction of both the *endo* and *exo* motifs.[5] Differential Scanning Calorimetry (DSC) showed a glass transition around 90 °C, before the onset of depolymerisation (**Figure 3B**).

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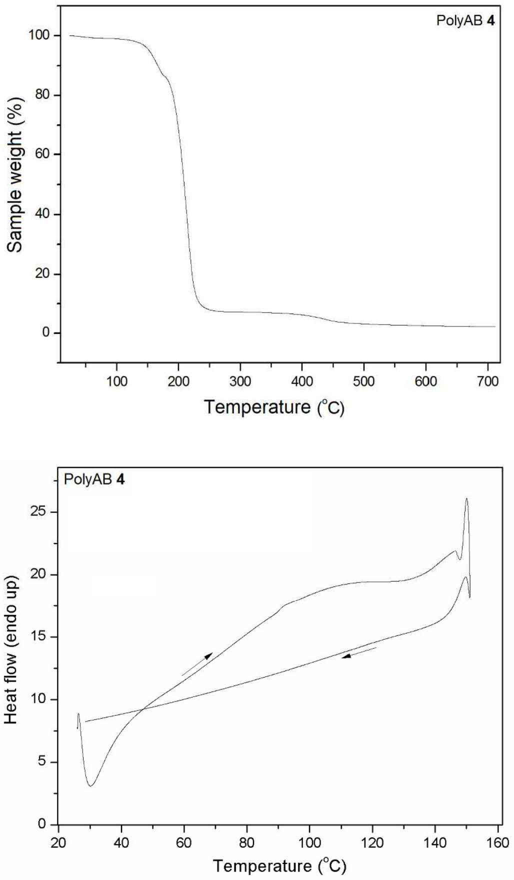

Figure 3. (a) TGA and (b) DSC thermograms of polymer 4.

The rigid regular structure of polymer 4 suggested the possible occurrence of partial crystallization, which was however not confirmed by X-ray diffraction analysis (**Figure 4**). This could be explained by the stereochemistry of the furan/maleimide adduct, present as *endo* and *exo* isomers, which would interfere with the formation of highly ordered macromolecular structures.

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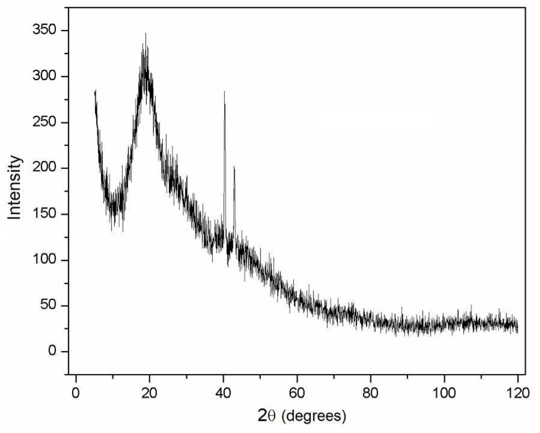

Figure 4. X-ray diffractogram of polymer **4.**

DSC was also used to measure the melting temperature of **5**, which appeared as a rather sharp endothermic peak centred at 94 °C, immediately followed by its DA exothermic polymerization in the molten state (**Figure 5**). These results are in accordance with monitoring glass capillary heating features. The AB monomer **5** was also characterized by mass spectrometry, which indicated the formation of dimers by the presence of a prominent $[M-H]^-$ (negative ion mode) peak at 353 mu.

It is important to emphasize that monomer **5** was found to be thoroughly stable at room temperature, i.e. no evidence of its spontaneous DA self-polymerization was detected within more than one-year storage in its crystalline form.

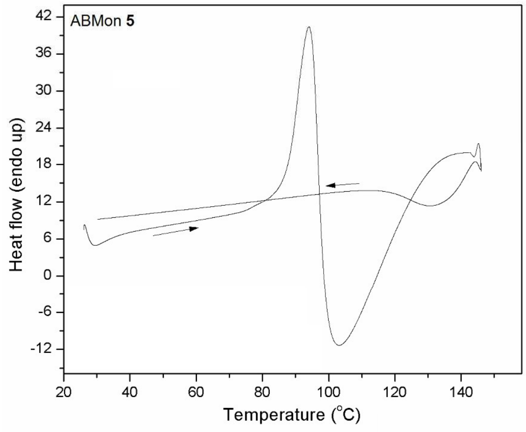

Figure 5. DSC thermogram of monomer **5**.

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Polymerizations of the isolated **5** were conducted with a 0.3M solution in TCE-d_2, kept at 60 °C. A typical ^{1}H NMR spectrum acquired during this process is depicted in **Figure 6**.

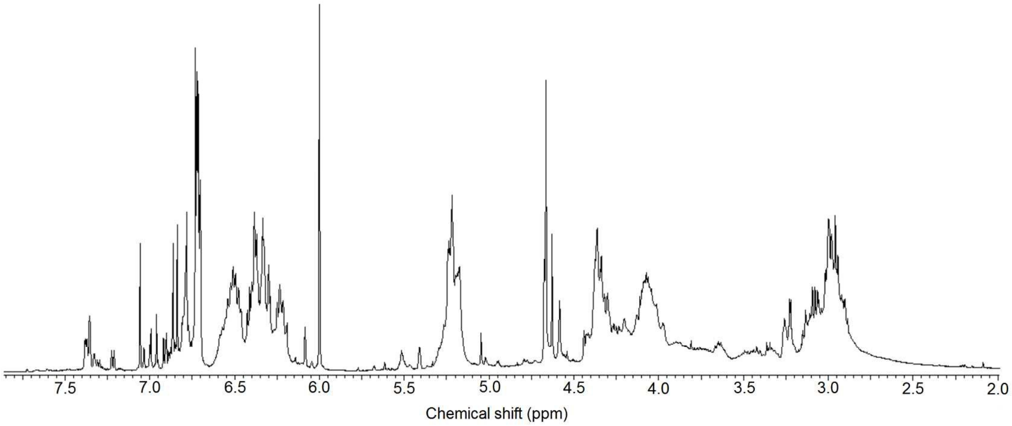

Figure 6. ^{1}H NMR spectrum of the initial phase of the AB-Mon **5** polymerization.

The evolution of the spectral features strongly indicated the progressive formation of the DA polymer, by the appearance of the broader peaks already characterized in the initial PolyAB spectrum (Figure 2) and the corresponding decrease in the intensity of the peaks associated with both furan and maleimide moieties. It was possible to estimate an approximate value of degree of polymerization (DPn) of PolyAB by calculating the ratio between the integration of the peaks arising from the protons of the monomer units positioned within the polymer chain (adducts) and those from terminal moieties (unreacted furan and maleimide rings). Following this approach, the ratio between the integration of the peaks ranging from 5.09 to 5.36 ppm, which correspond to the hydrogen atoms of the furan-maleimide adducts and the peaks ranging from 7.27 and 7.41 ppm, attributed to terminal furan motifs, led to a DPn of approximately 10 (Mn ~1800 Da) for homogeneous polycondensations, i.e. before polymer precipitation took place. Indeed, at the advanced stage of all these experiments a precipitate appeared. Its characterization confirmed that it bore the same structure as the polymer being generated, indicating that saturation had been reached and thus suggesting that higher DPs could not be attained under those conditions. Other solvents and initial monomer concentrations did not give rise to improved solubility. These observations were in tune with the difficulty mentioned above in preparing adequate solutions for GPC analysis and reiterated the polymer stiffness interpretation.

Although the synthesis of this compact AB-type DA monomer did not provide the opportunity to synthesize high-DP homopolymers, its utilization as a *comonomer* in systems involving other more flexible AB structures, as in the case of plant oil-based monomers,[6] opens the way to random and block copolymers with tuneable properties, such as glass transition temperature and mechanical performances. This possibility is being pursued.

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Notes and References

*The authors declare no competing financial interest.

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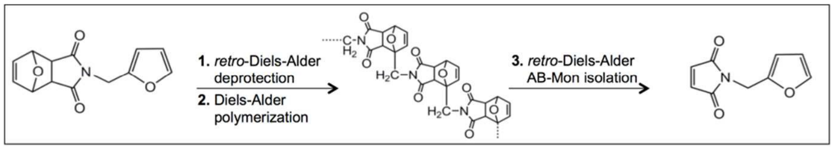
GRAPHICAL AND TEXTUAL ABSTRACT



An original approach to prepare and polymerize the shortest Diels-Alder AB monomer.