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Self Healing Polymers Prepared via Living Radical Polymerisation

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Diels Alder chemistry has been used to synthesise polymerisation initiators and a dimethacrylate cross-linker that exhibit efficient cleavage and reformation; *self-healing*. The initiators were prepared using **(3)** as an intermediate, and reacting this with furfuryl alcohol to afford **(7)** and 9-anthracene methanol to yield initiator **(8)**. The former exhibited excellent cleavage properties (M_n 12 000 g mol^{-1} to 6 500 g mol^{-1}) and reformed at an efficiency of 50% (M_n 8 900 g mol^{-1}). The initiator made using an anthracene derivative, initially indicated that retro Diels Alder was not occurring with no change in the NMR or GPC data. An excess of a rhodamine based dienophile was added to capture any cleaved anthracene-terminated polymer, with results indicating that the polymer is cleaving and reforming upon the cooling cycle. Similar results were evident in an arm frist star, made using a Diels-Alder based dimethacrylate crosslinker. Little cleavge was show initially, however addition of the tag gave a siginficant reduction in M_w (7 080 g mol^{-1} to 5 300 g mol^{-1}) and M_w/M_n (1.78 to 1.26).

1. Introduction

Self healing materials are inspired by biological systems where damage leads to an automatic healing response,[1] for example, the self repair of cuts and bruises on the human body. The application of this philosophy to polymers and materials is relatively new but gaining in interest for a number of potential applications.[2,3] Synthetic polymers often have a limited lifespan with a tendency to damage or degrade over time due to constant stresses and strains. This is driving the development of polymeric materials that can self heal, either as an effect of an external stimuli or, ideally by an auto-response.[3] In conventional materials damage first occurs at the microscopic level and repair at this level is essential to restore the full mechanical properties, as opposed to macroscopic repair with adhesives, etc. For polymers this has been achieved by both irreversible repair, i.e.by incorporating microcapsules containing reactive monomer into a thermoset matrix[2] or by including an element of reversibility, either covalent or non-covalent, into cross linked polymers.[3]

Diels Alder cycloadditions (DA) are a convenient route for the formation of carbon-carbon bonds via a facile reaction under undemanding conditions that fulfills the requirements of a “click” reaction.[4] Diels Alder cycloadditions are thermoreversible reactions[5] and this feature has been exploited in the preparation of self healing polymers carrying functionalities, either as the polymer chain-end or in the repeating units.[3] Furthermore, the reverse DA reaction does not involve free radicals, thus avoiding many side reactions that might prevent reformation.[6] Diels Alder moieties were first incorporated into polymers by Stevens and Jenkins.[7] Subsequently Saegusa and coworkers developed a thermally “mendable” polymeric DA network.[8] A Diels Alder - crosslinked polymer synthesized for the specific use of self healing was prepared by Wudl *et al*. in 2003, using furan- and maleimide-based monomers crosslinking along the polymer backbone.[5] In this study it was shown that fractured polymer materials, heated to 120 °C, exhibited 83 % recovery of the polymers original strength. Crucially, this fracture/repair cycle could also be repeated, making this the first real DA polymeric system exhibiting a thermally responsive self healing behavior.

This route to self healing polymers is applicable to composite materials and large crosslinked networks. Advances in controlled radical polymerization (CRP) allow for the synthesis of functional polymers with excellent control over molecular weight, molecular weight distribution, architecture and incorporation of functionality. The introduction of a range of techniques, ATRP,[9-11] RAFT[12] and NMRP[13] give the polymer chemist a great deal of control of polymer properties. Herein, we report the use of a living radical polymerization to synthesize a self healing polymer. The chemistry employed is efficient and relatively simple and has allowed for the design of cleavable linkers that contain polymerisation initiators In addition, a DA based cross-linker that can be employed in the synthesis of arm first stars is reported.

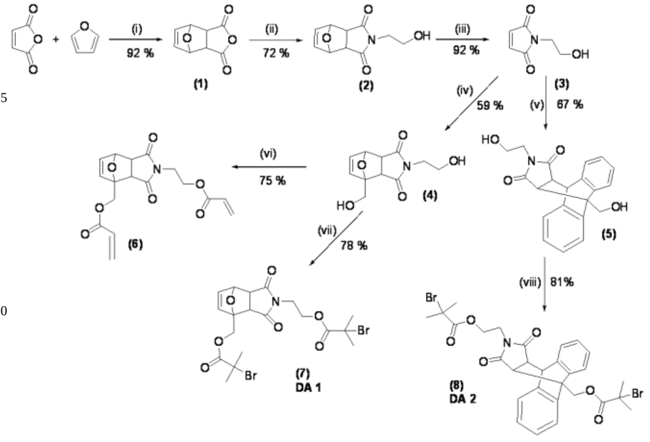
In this present study we report the synthesis of novel well-defined linear and star methyl methacrylate (MMA) polymers bearing DA adducts within their macromolecular backbone and a preliminary evaluation of their ability to cleave and reform under external thermal stimuli.

2. Results and Discussion

Synthesis of initiators and crosslinking agents

The synthetic protocol developed for the synthesis of the initiators **DA1** and **DA2** is shown in **Scheme 1**. The Diels-Alder adduct **(1)** was prepared by heating a suspension of maleic anhydride in furan and toluene at 120 °C for 24 h to give, after crystallisation exclusively the *exo* isomer. A solution of **(1)** in methanol and triethylamine (TEA) was subsequently treated with monoethanolamine at 0 °C, and slowly heated to 67 °C, as described by Hung et al.,[14] affording, after crystallisation, the alcohol **(2)** in 72 % yield. This was then subjected to a retro Diels-Alder process in refluxing toluene for 24 h, to give the maleimide containing alcohol **(3)**, which served as a versatile intermediate for the synthesis of both initiators **DA1 (7)** and **DA2**

(8). Initiator **DA1** was obtained by treatment of **(3)** with furfuryl alcohol to give diol **(4)**, which was esterified with 2-bromoisobutyryl bromide in THF/TEA, to give, after flash chromatography, the difunctional initiator **DA1 (7)** in 78 % yield. **DA2 (8)** was prepared in an analogous way, by treating **(3)** with 9-anthracenemethanol followed by esterification of the resulting diol **(5)** with 2-bromoisobutyryl bromide in THF/TEA, to give **DA2 (8)** in 81 % yield. The diacrylate **(6)**, employed later in this study as a thermoresponsive crosslinking agent, was prepared in a 75 % yield, again from **(4)**, using acryloyl chloride and TEA in anhydrous dichloromethane.



Scheme 1 *Reagents and conditions* (i) Toluene, 80 °C (ii) ethanolamine, Et_3N, MeOH, 0 °C to 70 °C (iii) toluene, reflux, 24 h (iv) furfuryl alcohol, benzene, reflux. (v) anthracenemethanol, toluene, reflux (vi) acryloyl chloride, dichloromethane, 0 °C – 25 °C. (vii)+(viii) 2-bromo isobutyl bromide, Et_3N, 0-25 °C, THF.

Polymerization

Linear poly(methyl methacrylate) (PMMA) was prepared by polymerisation, using **DA1 (7)** or **DA2 (8)** as the initiators with Cu(I)Br / pyridine imine ligand as catalyst.[15] Polymerisation in relatively non-polar/coordinating solvents are typically carried out between 70 °C and 90 °C; in the present case the tendency of the **DA1** difunctional initiator to dissociate on heating (DSC analysis of **DA1** at 5 °C per minute, suggested retro Diels-Alder dissociation occurring at ca. 120 °C, see ESI) prompted us to lower the polymerisation temperature to 50 °C. All polymerisations proceeded as expected, showing relatively linear first-order kinetic plots and linear increase of M_n with conversion (Fig. 1), affording well-defined polymers of tunable chain size and narrow molecular weight distributions determined by GPC analysis using chloroform/TEA 95:5 as the eluent (Table 1).

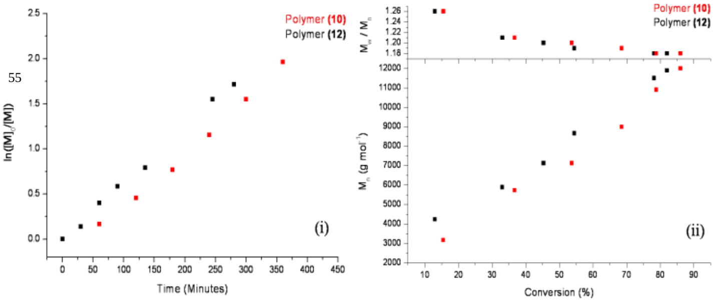


Fig. 1 (i) Comparison of rates for polymers **(10)** (50 °C) and **(12)** (70 °C). (ii) M_n vs. conversion for the polymers **(10)** and **(12)** .[Cu(I)Br]/[ligand]/[initiator]$_0$/[MMA]$_0$ 2:4:1:100

polymer	initiator	M_n (kDa)^a	PDi^a
(9)	**DA1 (7)**	5.4	1.11
(10)	**DA1 (7)**	12.0	1.12
(11)	**DA1 (7)**	54.7	1.15
(12)	**DA2 (8)**	11.9	1.18

Table 1. Linear polymers prepared in this study.

The ability of polymers **(9)**-**(12)** to respond to thermal stimuli was investigated. The ^{1}H NMR signals for the Diels-Alder derived polymer feature a very distinctive pattern of signals, which can be easily distinguished from the dissociated polymer (Fig. 2).

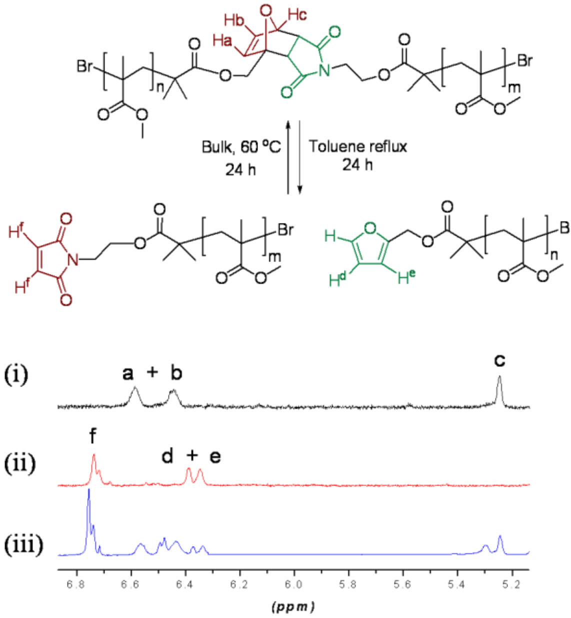


Fig. 2 ^{1}H-NMR of polymer **(10)** (i) prior to heating (ii) cleaved polymer following heating and (iii) reformed polymer.

Following thermal treatment of polymers **(9)**-**(11)** under reflux in toluene over 24 h a completely different pattern of peaks in the ^{1}H NMR was observed and each signal was easily identified, indicating that a retro Diels-Alder process occurred efficiently under these conditions, to give *N*-maleimide (6.89 ppm) and furfuryl ester (6.36 and 6.39 ppm)-terminated polymers. After removal of the solvent under reduced pressure, the reaction mixture was heated at 60 °C for 24 h. NMR analysis of the resulting reaction mixture revealed that approximately 50 % of the Diels-Alder linker had reformed under these conditions (5.22, 6.45 and 6.57 ppm). This value is comparable to the 59 % yield observed for the analogous cycloaddition in which the maleimide alcohol **(3)** and furfuryl alcohol were converted into the adduct **(4)**. It is noted that previous reports in the area of self healing polymers often reported healing efficiencies of 50%, which were found to be sufficient for significant recovery of mechanical properties.[16] In the ^{1}H NMR spectrum two new signals at 6.49 and 5.3 ppm, not previously seen neither in the spectra of the DA polymers **(9)-(11)** nor in the maleimide- and furan-terminated polymers were obtained after the retro-Diels Alder process (Fig. 2). NMR investigation and comparison with data reported in the literature[17] indicated that the reformed polymer was a mixture of *endo* and *exo* isomeric Diels-Alder linkers.

The GPC traces confirmed a significant proportion of polymer reformation (Fig. 3), although a quantitative assessment of the yields for this Diels-Alder process was not extrapolated from this data due to partial overlapping of the peaks of the cleaved and non-cleaved polymers. As expected, the molecular weight of the former was found to be was approximately half that of the original polymer, whilst, upon reformation, the molecular weight increases, as expected. The PDi's also increased upon Diels-Alder linker reformation, which was due to partial peak overlap, Table 2.

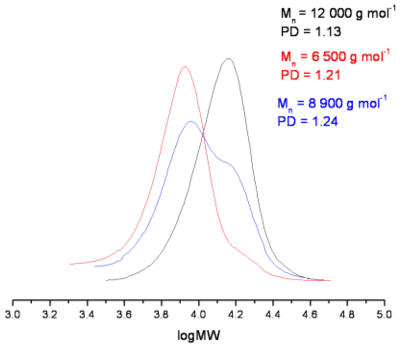


Fig. 3 GPC data of (i) polymer **(10)** (black) (ii) cleaved polymer (red) and (iii) the reformed polymer (blue), under the conditions described in Fig. 2.

Polymer	M$_n$ (kDa)^a	M$_w$ (kDa)^a	M$_w$/M$_n$^{a}	[η]^b
(9)	5.40	5.99	1.11	-
cleaved	2.76	3.25	1.18	-
reformed	4.10	4.96	1.21	-
(10)	12.0	13.5	1.12	0.072
cleaved	6.5	7.81	1.21	0.041
reformed	8.9	11.0	1.24	0.052
(11)	54.7	62.9	1.15	-
cleaved	28.4	34. 7	1.22	-
reformed	42.0	52.0	1.24	-

Table 2. GPC data for polymers **(9)-(11)**. ^{a} Determined by GPC analysis using THF/TEA 95:5 (vol/vol) as the mobile phase and PMMA as calibrants; ^{b} Intrinsic viscosities were measured for polymer (**10**) and its cleaved/reformed derivatives.

Polymers prepared from the difunctional initiator **DA1 (7)** showed excellent cleavage/re-healing properties. Polymer **(12)**, prepared from the difunctional initiator **DA2 (8)**, was introduced as maleimide-anthracene molecules are known to undergo Diels-Alder process in a facile manner. Dag *et al* showed that star polymers could be synthesised via a Diels-Alder click reaction.[18] An arm first core was grown first with an anthracene based initiator. Subsequently a protected maleimide functional polymer was introduced, and a highly efficient deprotection followed by click reaction to the anthracene core in one pot occurred.[18] However, subsequent deprotection of these polymers was not reported. This suggested either that the retro Diels-Alder did not occur, or that the process did occur to a certan extent, but the Diels-Alder linkers subsequently did reform, upon cooling or directly at the temperature employed for the deprotection, which is common in self healing systems.[5] The polymers formed from **DA1 (7)** did not exhibit reformation upon cooling.

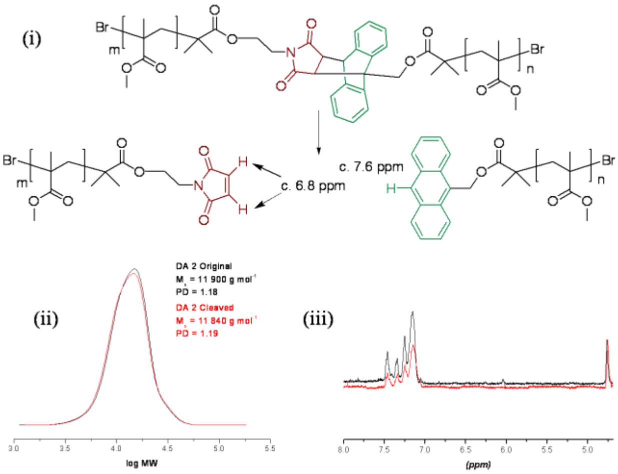


Fig. 4 Attempted deprotection of **(12)** in DMSO at 200 'C (i) reaction scheme (ii) GPC data and (iii) partial ^{1}H-NMR spectra before and after the attempted retro Diels-Alder polymer cleavage.

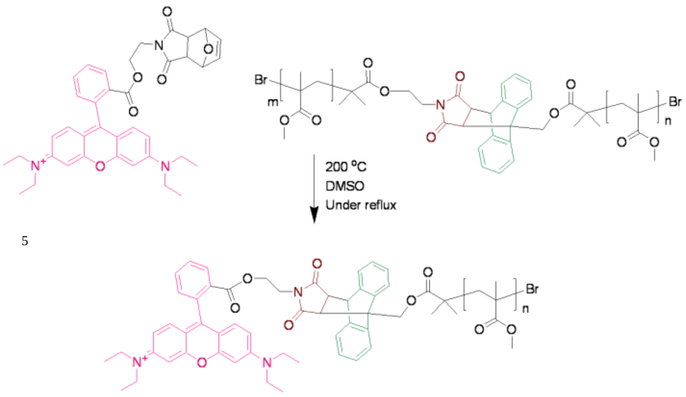


Fig. 5 The expected product **(12)** cleaved during the heating process. This product could then be detected by UV GPC.

To investigate whether the anthracene-maleimide linker was cleaving and then reforming upon cooling, an excess of a dienophile was added to capture any cleaved anthracene-terminated polymer. For this purpose, we synthesised a maleimide-containing rhodamine B probe (Fig. 5). Retro Diels-Alder cleavage was attempted in the presence of 50-fold molar excess of the rhodamine tag, in refluxing DMSO. The tag was introduced as its furan adduct which released the desired maleimide-containing fluorophore *in situ*, upon heating. Complete cleavage, as in the case of polymers **(9)-(11)**, should halve the M_n. In this case the M_n decreased by only 20%, suggesting that approximately a fifth of the linker had effectively cleaved throughout the process. Evidence that exchange has taken place came from GPC with UV-Vis detection at λ = 550 nm, the resulting material was now clearly detected. (Fig. 6). The starting material **(12)** has no absorption at this wavelength. This suggests that the anthracene-maleimide linker in **(12)** has a higher thermal stability than the furan-maleimide present in **(9)-(11)**, and that any cleaved materials formed upon heating **(12)** at 200 °C were able to undergo Diels-Alder cycloaddition upon slow cooling back to ambient temprature.

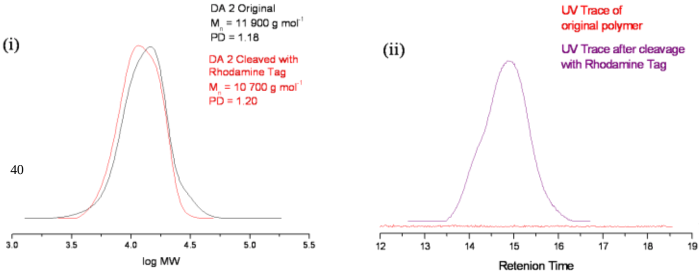


Fig. 6 Cleavage of **DA2** polymer monitoed by GPC with (i) DRI detection and (ii) UV detection showing no absorbance in the original polymer, and a peak following cleavage and addition to the with the rhodamine tag

In order to investigate the applicability of the approach the study was extended to star polymers. A difunctional crosslinker monomer containing a substituted furan/maleimide Diels Alder adduct was synthesized for this purposes. Due to structural similarities with polymers **(9)-(11)** obtained from the initiator **DA1 (7)** we expected the retro Diels-Alder cleavage of the crosslinker to occur to a relatively large extent.

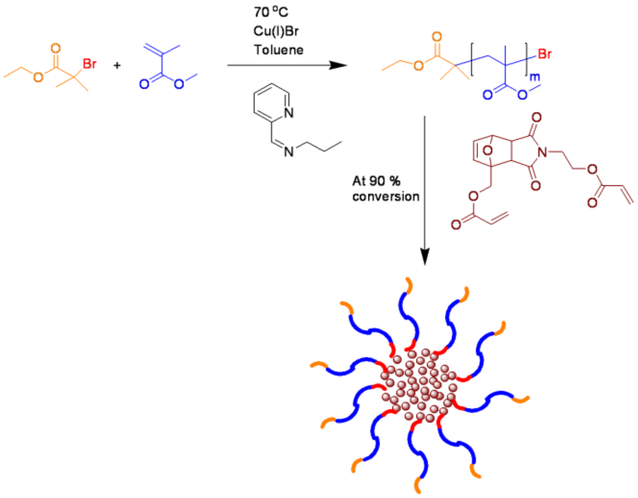


Fig. 7 Synthesis of star polymer **(13)**

Refluxing **(13)** in toluene for 24 hours, suggested that a small amount of cleavage takes place with a shoulder corresponding to a lower molecular weight material detected in the GPC chromatogram, fig. 8. As polymers **(9)-(11),** were easily cleaved under analogous reaction conditions , it was suspected that significant proportion of the star cleaves and reforms within the cooling cycle. In this system complete cleavage of the star was expected to afford lower molecular weigh materials with narrower PDI's. One possible explanation for this behaviour was that in a crosslinked network a less than quantitative retro Diels-Alder process would caused the diene/dienophile cleaved moieties to remain spacially close to each other which would favour the reformation of the Diels-Alder linkers.

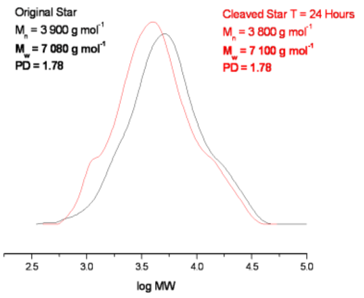


Fig. 8 GPC data before and after attempted cleavage of the star polymer. Evidence that some cleavage has occurred is apparent from the appearance of low molecular shoulder in the cleaved product

In order to investigate this the maleimide functionalised rhodamine trapping agent was added in the reaction mixture.In this case the M_w of the star polymer polymer was reduced dramatically, and the PDi decreased from 1.78 to 1.26 indicating that the majority of the crosslinker units was effectively cleaving under these conditions.

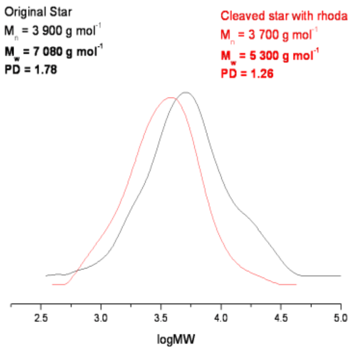


Fig. 9 GPC data before and after cleavage woth the rhodamine tag, showing a vast reduction in the polydispersity and Mw data.

At this stage it is still not clear whether this system did reheal upon cooling or weather the Diels-Alder linkers were constantly cleaving and reforming. The cleaving and reforming throughout the heating cycle was confirmed by high temperature GPC at 140 °C, with 1,2,4 – trichlorobenzene as eluent, whch showed little change from the original polymer. (see supporting info).

3. Summary

Two polymerisation initiators and one crosslinker were prepared using DA chemistry. **DA1** exhibited exceptional cleavage properties, with 50 % reformation occuring upon the reheating cycle. However, the facile nature in which this linker cleaved can be a problem for practical applications. Changing the alcohol to 9-anthracenemethanol gave the Diels-Alder linkage higher thermal stability. The forward DA reaction is highly efficient when using 9-anthracenemethanol, and the small amount of cleavage occuring is reforming in the cooling cycle. To investigate other polymer archtitecures, the same principle was applied to arm first stars, however, this time it was the shear quantity of linkages that enabled the Diels Alder bond to constantly cleave and reform throughout the heating process

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Notes and references

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† Electronic Supplementary Information (ESI) available: Full experimental details and additional characterisation data. See DOI: 10.1039/b000000x/

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