Fast and catalyst-free hetero-Diels–Alder chemistry for on demand cyclable bonding/debonding materials†

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A new dithioester possessing a cyano Z-group (cyano-dithioester (CDTE)) has been synthesized via a 2-step, one-pot reaction. The cyano-substituted dithioester has been found to undergo fast reversible hetero-Diels–Alder (HDA) reactions at ambient temperature, without the need for a catalyst, as demonstrated by ESI-MS and UV-Vis experiments. To apply the bonding/debonding on demand system to materials science, a cyano-dithioester di-linker was synthesized and employed as a di-functional dienophile in a HDA-based polymerization reaction with a bis-cyclopentadiene polymer. The reversible bonding of the polymer systems were demonstrated by on-line UV-Vis spectroscopy, on-line NMR spectroscopy, and on-line high temperature DLS, as well as via GPC in situ trapping experiments and high-level ab initio molecular orbital calculations.

One very promising heat triggered reversible reaction that provides the advantages of atom economy, functional group tolerance, and high yields is the Diels–Alder (DA) reaction. Pioneered by Wudl and coworkers, the field of DA-based materials has been enriched by many contributions from a number of working groups.13–20 The first and most commonly studied DA pair for reversible bonding applications is N-maleimide/furan.16,21–24 Showing reversibility above 120 °C, this DA pair is suitable for a large variety of applications, which require moderately low cycling temperatures. Unfortunately, diene/dienophile pairings with lower retro-DA (rDA) temperatures are scarce. This has prompted renewed efforts to develop new DA pairings capable of fast debonding at lower temperatures. For example, Lehn and coworkers synthesized a network, containing a DA pair (i.e., tricyanoethylene-carboxylate/fulvene), which shows a dynamic equilibrium at ambient temperature.25 Our group has also developed a low temperature reversible covalent chemistry, employing activated dithioesters as dienophiles in hetero-DA (HDA) based polymerization reactions.6–13 Unlike maleimide/furan DA chemistry, HDA chemistry is fast in both the forward and reverse directions. However, until now the forward reaction has required the addition of a Lewis acid (e.g., trifluoroacetic acid or ZnCl2) to proceed rapidly, if water is not utilized as the solvent.25,26 To avoid the need for a catalyst while maintaining high reaction rates, it is necessary to synthesize a dithioester that is intrinsically activated for HDA reactions. Such activated dithioester moieties can be generated by utilizing a Z-group that is even more electron-withdrawing than those employed previously (i.e., pyridine or phosphonate) because the more electron-withdrawing the Z-group, the more electron deficient the C=S bond and, therefore, the better the

Introduction

The biological phenomenon of wound healing, which increases the lifetime of humans, has inspired many working groups to dedicate their research to overcoming the challenge of transferring similar properties to synthetic materials.1–3 Current efforts primarily focus on designing materials that are based on reversible/dynamic covalent bonds, able to mend themselves through opening and closing links within the material. Depending on the physical and chemical nature of the material designed, forming and breaking of the covalent bonds proceed either autonomously or in the presence of an external stimulus. Examples of stimuli that have been employed to trigger the cycling of covalent bonds include heat,4–7 light,8,9 pH,10,11 and redox chemistry.12

†Electronic supplementary information (ESI) available: Synthetic procedures, SEC ESI-MS, UV-Vis, DLS and NMR data, and a complete description of the computational results and procedures. See DOI: 10.1039/c3py00476g

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C=S bond acts as a dienophile. Fortunately, there is evidence suggesting that a cyano group may serve our desired purpose. The high reactivity of cyanodithioesters (CDTE) toward several dienes, employed in DA reactions to obtain sulfur-containing carbohydrates, was previously reported by Vyas and Hay.27–29 Despite the significant potential of CDTE chemistry, only a few research groups have further explored it, which may be attributed to the complex synthesis associated with generating molecules substituted with cyanodithioate units.

Herein, we present a novel synthetic strategy for the synthesis of two, hitherto unknown CDTE compounds (1a and 1b), as well as a DA study of cyclopentadiene (Cp) reacted with a CDTE end-capped poly(ε-caprolactone) (PCL) 2. The fast, catalyst free cyclability of the DA reaction between a CDTE and Cp was initially studied by UV-Vis spectroscopy and electrospray ionization-mass spectrometry (ESI-MS) for a small molecule model, before progressing to polymeric systems. In order to apply this reversible chemistry to a polymeric material, a CDTE based di-linker was generated, which was reacted with a bis-Cp polymer to form a linear polymer. Size exclusion chromatography (SEC), on-line (in situ) UV-Vis spectroscopy, on-line (in situ) high temperature dynamic light scattering (HT-DLS), as well as on-line temperature dependent 1H NMR spectroscopy measurements revealed the repeatedly reversible nature of the DA-based linear polymer, when going from ambient temperature to 100 °C.

**Results and discussion**

In contrast to many other dithioesters, it is not possible to simply introduce the CDTE into a molecule by performing a nucleophilic substitution reaction with the cyano-dithioate salt. As a result of the electron deficient character of the thiocarbonyl group, this group is vulnerable to attack by any nucleophile, such as the leaving group (LG). Such an attack initializes the dimerization process reported by Bähr and Simmons (Scheme 1, top pathway).30–32 To circumvent the problem, a new procedure was developed in which three equivalents of Cp were added during the cyano-dithioate nucleophilic substitution reaction. The highly reactive Cp functions as a trapping agent for the CDTE formed *in situ* and, therefore, protects it against dimerization (Scheme 1), allowing it to be purified by flash column chromatography. The *in situ* trapping also serves to protect the thiocarbonyl group from oxidation. Therefore, the protected CDTE is stable in air, at ambient temperature and in the presence of light, which is not usually the case for dithioesters.31

By employing the synthesis strategy described above, two trapped CDTEs, 1a and 1b, were synthesized (Scheme 1, bottom pathway). Following purification, 1a was utilized in the ring opening polymerization (ROP) of ε-caprolactone to yield a protected CDTE end-capped PCL, 2, with a number average molar mass (Mn) of 2000 g mol⁻¹ and a molar mass dispersity (Đ) of 1.20.

With 2 in hand, the rDA deprotection reaction was first evaluated by temperature-dependent on-line UV-Vis spectroscopy. This analytical technique was selected because in contrast to the protected CDTE the deprotected species, 3, undergoes the strong π−π* transition characteristic of dithioesters and thus, it absorbs UV light. The absorbance of 2, dissolved in toluene in a sealed cuvette, at 347 nm was recorded as the temperature was cycled between 40 °C and 100 °C eight times (Fig. 1). As expected, at elevated temperatures the absorption at 347 nm increases, implying that the DA reaction equilibrium is shifted towards 3 and Cp (i.e., the rDA products).

Importantly, the UV-Vis data shown in Fig. 1 clearly demonstrate the feasibility of repeated cycling between 2 and 3. Although a slight decrease in the maximum absorption signal is observed over time, chemical hysteresis was discarded as the source for the slight signal decrease since UV-Vis spectra of the CDTE species (i.e., 2 and 5) showed no decrease in absorption intensity after the cycling experiments relative to the initial spectra collected prior to the start of the experiment (i.e., time = 0) (Fig. S1†). Therefore, it was concluded that the decrease in the

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**Scheme 1** Dimerization process of the CDTE intermediate, initialized by the attack of the leaving group (LG) in the absence of a trapping agent (top pathway). Synthesis of protected CDTE (1a and 1b) by reacting the intermediate *in situ* with Cp, which acts as the trapping agent (bottom pathway).

**Fig. 1** Temperature dependent UV-Vis spectroscopy data of the trapped CDTE 2 in toluene during the cycling between 40 °C and 100 °C (heating/cooling rate was 1 °C min⁻¹). The absorption was recorded at 347 nm. A baseline correction was applied according to a literature procedure.*
absorption maximum over time resulted from a baseline shift, attributed to detector drift over time and temperature. The UV-Vis study thus demonstrates the on demand cyclability of the CDTE DA/rDA reaction.

To quantitatively assess the rDA reaction of 2, the kinetics of a diene exchange reaction were analyzed by ESI-MS. The protected CDTE 2 was heated in toluene with two equivalents of 1,3-dimethylbutadiene (DMBD) (i.e., the diene to be exchanged with Cp). DMBD was chosen as the replacing diene because the corresponding DA products are known to have generally higher rDA temperatures than the DA products obtained from Cp. Consequently, the rDA reaction of the DMBD trapped CDTE functionalized PCL, 4, to form 2 could be avoided. In this experiment, the extent of diene exchange at 120 °C was assessed over time. Fig. 2 depicts the mass spectrum at 0 min of the diene exchange reaction of Cp against DMBD at 120 °C. The 0 min (i.e., ambient temperature) starting material spectrum suggests that a small amount of unprotected CDTE 3 exists in addition to 2. The presence of 3 in this MS spectrum can be explained by the fact that the rDA reaction occurs during the ESI-MS measurement. After 10 min the MS data evidence that the rDA reaction has proceeded to approximately 66% completion, which supports the notion that the CDTE deprotection occurs rapidly in the presence of DMBD. A completion, which supports the notion that the CDTE deprotection occurs rapidly in the presence of DMBD. Consequently, the rDA reaction of the DMBD trapped CDTE protected CDTE DA/rDA reaction. The cycling was performed in a NMR pressure tube with toluene-d8 as the NMR solvent at a substrate concentration of 0.02 mol L−1. Fig. 3 shows a zoom into the region between 5 and 7 ppm of the NMR spectra of 5 at different temperatures. In agreement with the UV-Vis study, the NMR spectra at elevated temperatures revealed additional signals in the double bond region occurring from free Cp, formed by the rDA reaction. The additional signals started to rise already at 70 °C and increased with the rising temperature. Unfortunately, it was not possible to increase the temperature above 130 °C due to device limitations. Subsequent to heating to 130 °C, the sample was cooled to 25 °C, no longer showing free Cp signals in the NMR spectrum. Additionally, the same peak intensity of free Cp was reached, compared to the spectra recorded prior to heating to 130 °C and cooling to 25 °C, when heated again to any temperature above 70 °C. Such cycling experiments were carried out several times with arbitrary temperatures between 70 and 130 °C and every time the same Cp intensity at the given temperature was detected. This finding implies that 5 is 100% cyclable between 130 °C and 25 °C, and is stable at the elevated temperatures that are necessary for the polymerization reaction and for the cycling process.

As further confirmation of its reversibility, we additionally conducted high-level ab initio molecular orbital calculations of the two-step retro-Diels–Alder reaction of 5 in toluene solution over a wide temperature range using the same methodology described previously (refer to section 4 in the ESI†). Our predicted concentration profiles of all 4 species are shown in Fig. 3b where it is clear that the computational results are in excellent agreement with the experiment, providing mutual verification of the accuracy of the calculations and the absence of competing side reactions in the experimental system. The first retro-Diels–Alder reaction becomes apparent above 50 °C, while the loss of the second Cp to form the bis-CDTE species becomes significant above 150 °C.

Before utilizing the novel di-linker 5 in a polymerization reaction, its ability to switch between the protected and deprotected state, without undergoing degradation, was explored via temperature dependent 1H NMR spectroscopy. The advantage of on-line high temperature 1H NMR spectroscopy (HT-NMR) is that it combines the qualitative proof of the on-line UV-Vis experiment with the quantitative findings of the diene exchange studies analyzed by ESI-MS, giving an additional on-line view of the DA reaction. The cycling was performed in a NMR pressure tube with toluene-d8 as the NMR solvent at a substrate concentration of 0.02 mol L−1. Fig. 3 shows a zoom into the region between 5 and 7 ppm of the NMR spectra of 5 at different temperatures. In agreement with the UV-Vis study, the NMR spectra at elevated temperatures revealed additional signals in the double bond region occurring from free Cp, formed by the rDA reaction. The additional signals started to rise already at 70 °C and increased with the rising temperature. Unfortunately, it was not possible to increase the temperature above 130 °C due to device limitations. Subsequent to heating to 130 °C, the sample was cooled to 25 °C, no longer showing free Cp signals in the NMR spectrum. Additionally, the same peak intensity of free Cp was reached, compared to the spectra recorded prior to heating to 130 °C and cooling to 25 °C, when heated again to any temperature above 70 °C. Such cycling experiments were carried out several times with arbitrary temperatures between 70 and 130 °C and every time the same Cp intensity at the given temperature was detected. This finding implies that 5 is 100% cyclable between 130 °C and 25 °C, and is stable at the elevated temperatures that are necessary for the polymerization reaction and for the cycling process.

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Next, the DA based AA–BB step-growth polymerization of the CDTE di-linker and a readily available bis-Cp polymer (CP2=P(BOA-nBA)); Mn = 13 000 g mol−1, Dm = 1.6) was performed in the bulk to mimic a self-healing process that would be expected of such an applied material. First, a homogeneous bulk mixture...
of the building blocks was generated by dissolving the building blocks in dichloromethane, stirring the solution for 1 min, and removing the solvent. The bulk material was heated to 120 °C in an open flask for 1 h after which it was slowly allowed to reach ambient temperature, yielding the HDA based polymer 6. An elevated temperature was required for the polymerization reaction with 5 to remove (i.e., via rDA chemistry) the Cp protecting group, just as a high temperature was necessary for the diene exchange study. The polymerization temperature was selected based on the fast reaction rates observed at 120 °C in the diene exchange study.

Further confirmation that heating is required to deprotect the CDTE di-linker in order to permit polymerization was obtained by simply analyzing a 1 to 1 molar mixture of 5 and Cp₂-P(BoA-nBA), prior to heating, by SEC. As expected, the chromatogram obtained demonstrated that the building blocks do not undergo any reaction at low temperatures since their corresponding molecular weight distributions remain unchanged (Fig. 4). The smaller peak appearing at higher retention times correlates well with 5 and the high molecular weight polymer distribution (i.e., lower retention times) associated with the larger peak is attributed to Cp₂-P(BoA-nBA). Note that the high molecular weight (i.e., low retention time) shoulders associated with the Cp₂-P(BoA-nBA) peak can be explained by the slow Cp-Cp dimerization that occurs over time despite storing the Cp₂-P(BoA-nBA) at –20 °C. Due to the Cp dimerization reaction, the polymer distribution changes slowly over an extended period of time making it challenging to accurately prepare a 1 to 1 ratio of the building blocks, with respect to their available functional groups. Once 5 was deprotected, in situ, the deprotected 5 was subsequently available to react further with other dienes present in the mixture (i.e., Cp₂-P(BoA-nBA)) (Scheme 3). The polymerization reaction was allowed to proceed for an hour instead of thirty minutes because it is reasonable to assume that the polymerization process requires more time to achieve complete conversion, given the exchange of Cp against another Cp species and the nature of DA equilibrium. In addition to initializing the rDA deprotection process, the high temperature also permits the vaporization of Cp, which theoretically should drive the polymerization forward.

Without further purification, the polymer 6 was characterized by SEC and was found to have a $M_m = 2.5$ and a $M_n = 34,200$ g mol⁻¹, which corresponds to 79% conversion.

The near tripling of the $M_m$ of polymer 6 compared to the $M_n$ of Cp₂-P(BoA-nBA) and the increase of the $M_m$ from 1.6 to 2.5 indicate the success of the DA polymerization. Of course, the concern that the high molecular weight product results from the DA self-reaction of Cp₂-P(BoA-nBA) is real; however, a control reaction in which Cp₂-P(BoA-nBA) was heated to 140 °C for 12 h revealed no change in the $M_n$ of Cp₂-P(BoA-nBA). Moreover, the disappearance of IPDI-CDTE (i.e., 5) in the elugram of 6 clearly indicates that 5 is consumed during the polymerization process and incorporated into polymer 6. Despite the complete disappearance of 5, a shoulder at higher temperatures the calculated mol% of deprotected 5 is depicted. The resonance set disappears again when cooled below 70 °C. Increasing temperature (b) of all signals towards a lower field can be observed, which is associated with the increasing peaks the calculated mol% of deprotected can be seen increasing with the temperature. To the left hand side of the nance set disappears again when cooled below 70 °C.

![Image](52x357 to 282x729)

**Fig. 3** (a) $^1$H NMR spectra of 5 in deuterated toluene at different temperatures. Next to the DA product signals of 5, a set of signals that corresponds to free Cp can be seen increasing with the temperature. The to left hand side of the increasing peaks the calculated mol% of deprotected 5 is depicted. The resonance set disappears again when cooled below 70 °C. In addition, a general shift of all signals towards a lower field can be observed, which is associated with the increasing temperature. (b) Ab initio predictions of the temperature dependent concentrations of all four species present in the two-step retro-Diels-Alder reaction of 5. The corresponding experimentally observed concentrations of Cp are shown for the purpose of comparison. For further theoretical details see the ESI.†
retention times, that clearly corresponds to Cp₂-P(BoA-nBA), remains. The shoulder could not be eliminated by performing an optimization study of the equivalents of building blocks used in the DA polymerization. This result suggests that the remaining Cp₂-P(BoA-nBA) actually lacks both Cp end-groups, rendering it unreactive. Given that both atom-transfer radical polymerization and polymer Cp functionalization, which were utilized to synthesize Cp₂-P(BoA-nBA), commonly yield dead chains (i.e., non-Cp-functionalized polymer chains) the remaining Cp₂-P(BoA-nBA)-derived shoulder is less surprising. Considering the aforementioned results, the DA-based polymerization was considered to be successful.

The reversibility of the DA-based polymerization reaction of 5 and Cp₂-P(BoA-nBA) was assessed utilizing essentially the same procedure as that employed for the diene exchange study. A sample of polymer 6 was heated in toluene at 120 °C for 1 h with 10 equivalents of DMBD to trap all 5 that is released from the depolymerization reaction. SEC analysis of the product suggests that complete depolymerization, followed by the cycloaddition reaction, was achieved because the elugram is nearly identical to that of the mixture of 5 and Cp₂-P(BoA-nBA) prior to heating (Fig. 4). The only difference is a slight shift of the peak corresponding to 5 to slightly higher molecular weight values, which would be expected if DMBD were to be added to both sides of 5. In essence, the SEC elugram demonstrates that the IPDI-CDTE di-linker 5 can be regenerated at high temperatures and upon cooling will re-undergo a DA reaction if a diene is present (i.e., in this case DMBD). Naturally, it would be more satisfying to observe both the depolymerized product 6 in the absence of DMBD and the repolymerized 6 by SEC; however, repolymerization (the DA reaction) proceeds too rapidly to allow for the isolation and analysis of the untrapped depolymerized product. Therefore, the results of the trapping study are considered to be the next best option to demonstrate the reversibility of the system via SEC.

However, an on-line analysis technique, in addition to on-line UV-Vis experiments (see Fig. S4†), would finally demonstrate the cyclable properties of the DA polymer 6. Consequently, a temperature dependent dynamic light scattering (HT-DLS) experiment was performed to detect the shrinking (depolymerization) by heating and expansion (repolymerization) by cooling of the DA polymer. Therefore, a solution of 6 in 1,2,4-trichlorobenzene (TCB), with a concentration of 17 mg mL⁻¹, was cycled five times between 30 °C and 120 °C while recording the sample’s hydrodynamic radius (R_h) over time. Starting with an R_h of 2.43 nm, polymer 6 indeed shrunk when heated to 120 °C to 2.19 nm and expanded again when cooled to 30 °C. This constant switching behavior can be observed over the entire cycling process, which is depicted in Fig. 5b (solid line), giving final evidence of the reversibility properties of 6. Only slight fluctuations of about 0.05 nm can be observed at the end of the first and fourth cycle, yet such small values are within experimental error of DLS measurements. To assess the fluctuation, and especially to monitor the temperature dependence of the DLS results, a sample of Cp₂-P(BoA-nBA) was cycled under identical conditions (dashed line) to compare the obtained values as a reference to the results from polymer 6.

With an R_h of 1.83 nm at 30 °C and 2.00 nm at 120 °C, the R_h of the reference also shows a dependence on the temperature. This finding is expected, as the temperature has a significant influence on the coil dimension of polymers in solution. At higher temperatures the polymer usually expands and occupies a larger volume, resulting in a higher R_h value, while in a cooled state it collapses, which reduces the R_h. Whereas the R_h of the reference expands during heating and shrinks during cooling, the sample’s R_h behaves inversely, as is expected for rDA caused depolymerization and DA caused repolymerization. To support this finding and analyze the depolymerized structure, on-line HT-NMR analysis conducted on polymer 6 was carried out. Similar to the on-line HT-NMR experiments of 5, the spectra of 6 and Cp₂-P(BoA-nBA) were recorded in toluene-d₈ with a relaxation time of 1 s and 100 scans. With this set up, polymer 6 was cycled between 40 °C and 120 °C, similar to the HT-DLS experiment. As compounds 5 and 6 contain the same DA linkage, the proton signals of the double bond appear at 40 °C at the same shifts, 5.7 and 5.9 ppm (see Fig. 5a, top three spectra). The Cp end-group resonances of Cp₂-P(BoA-nBA) occur at 6.1 to 6.6 ppm. A spectrum of Cp₂-P(BoA-nBA) recorded at 120 °C revealed that the shift of the Cp end-group resonances is not influenced by the temperature. At 120 °C, polymer 6 showed the expected Cp signal between 6.1 and 6.6 ppm. When cooled to 40 °C, the Cp resonances vanished again, implying a full repolymerization of the end-groups. To confirm the reversibility also via the on-line HT-NMR technique, temperature cycling between 40 °C and 120 °C was repeated two times, yielding spectra which perfectly match each other when taken at the same temperature (Fig. 6a, bottom five spectra). To determine the percentage of debonding of 6 at 120 °C, the integral values of the DA product resonances and the Cp resonances were compared. With approximately 37 mol% of the starting material present at 120 °C, the system is well suitable for bonding/debonding applications. The debonding is even greater than that observed for the N-maleimide/furan system described by Chen et al. (12% debonding at 130 °C for 25 min), although it has to be noted that their values are obtained by

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**Fig. 4** Normalized SEC traces of the mixture of 5 and Cp₂-P(BoA-nBA) before heating (solid line, M_w = 7100 g mol⁻¹), polymer 6 (dotted line, M_w = 34 200 g mol⁻¹), and 6 heated in the presence of the trapping agent, 1,3-dimethylbutadiene (dashed line, M_w = 7400 g mol⁻¹).
solid state analysis of a network. Overall, the HT-NMR and HT-DLS results evidence the system’s reversibility, stability, lack of hysteresis, and structure of the debonded state. Moreover, the on-line HT-NMR results point to an extremely fast equilibrium that is reached already after 15 min.

In an effort to observe the depolymerized state of the DA polymer 6 and to understand the kinetics of the polymerization and depolymerization processes in detail, the reactions were additionally performed in a temperature dependent UV-Vis instrument, which permits the on-line observation of the evolution of the CDTE di-linker during the reactions. Each step of the reversible process, deprotection of 5, polymerization of deprotected 5 with Cp2-P(BoA-nBA), and depolymerization of 6, was analyzed separately.

To assess the kinetics of the deprotection step, an ambient temperature solution of 5 in toluene was injected into a 100 °C preheated cuvette containing a small amount of toluene and was immediately analyzed for absorption at 347 nm every 0.16 s.

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**Fig. 5** (a) Temperature dependent $^1$H NMR spectra of DA polymer 6. The stacked spectra depict a zoom into the double bond region of the starting materials for the DA polymerization 5 and Cp2-P(BoA-nBA) (two upper spectra) as well as the spectra of 6 recorded during the cycling between 40 and 120 °C (five lower spectra). The two cycles were executed in toluene-d$_8$ with a concentration of 20 mg mL$^{-1}$. (b) Temperature dependent DLS experiments of DA polymer 6 ($M_n$ = 34 200 g mol$^{-1}$) and Cp2-P(BoA-nBA) ($M_n$ = 13 000 g mol$^{-1}$). The traces in the diagram present the average of the $R_h$ of 6 (solid line) and Cp2-P(BoA-nBA) (dashed line) during the temperature (dotted line) cycling between 30 and 120 °C. TCB was employed as a solvent and both samples had a concentration of 17 mg mL$^{-1}$. The raw $R_h$ values, recorded during the temperature cycling, are depicted in Fig. S5.$^\dagger$

**Fig. 6** Absorption spectra, recorded at 347 nm, of all three processes presented on the left side, vs. time. The left side scheme (a) depicts the three processes. Spectrum (b) shows the deprotection of 5 by heating to 100 °C, (c) depicts the forward polymerization of deprotected 5 with Cp2-P(BoA-nBA) when heated to 110 °C and cooled to 20 °C, and (d) shows the depolymerization of 6 when heated to 100 °C. In the left scheme the polymerization process is schematically depicted.
for 5 min. The small amount of toluene that was heated with the cuvette served to drastically reduce the time required for the solution of 5 to attain 100 °C. The change in the absorption at 347 nm over time revealed that the deprotection of 5 is essentially already complete after 2.5 min. Next, the kinetics of (re)polymerization (to form 6) were characterized by first heating 6 to obtain the depolymerized state of the system and subsequently observing the repolymerization process by UV-Vis spectroscopy. More specifically, a solution of 6 in toluene was heated to 110 °C for 5 min, added immediately into the cuvette held at 20 °C in the UV-Vis spectrophotometer, and then analyzed for absorption at 347 nm, which was recorded every 0.16 s over 5 min. The results of this analysis, plotted in Fig. 6, indicate that the repolymerization of unprotected 5 with Cp2-P(Bb)(OAc-νBA) is even faster than the deprotection step with reaction completion occurring after just 1 min of cooling to 20 °C. Finally, characterization of the depolymerization step, which was performed by utilizing the same procedure as that employed to assess the deprotection reaction, suggests that depolymerization of 6 takes 4 min to reach equilibrium. The fact that this step is longer than either of the other two steps is not surprising considering the greater heat capacity of the DA polymer compared to the building blocks, Cp2-P(OAc-νBA) and 5.

All three traces demonstrate that none of the processes takes more than 5 min to reach the equilibrium state, which is indicated by the plateauing of the absorption signal. It should be noted that the y-axis scale differs for each graph because the molar concentration of the released CDTE-di-linker for each solution differed. Additionally, it is proven by on-line HT-NMR that 6 is not 100% depolymerized at 100 °C, instrument limitations prevented the characterization of the depolymerization process at higher temperatures. Regardless, the entire process of de- and re-polymerization at 100 °C takes a total of only 5 min. It is probable that the reaction kinetics would be very similar at higher temperatures. This finding supports the notion that the novel CDTE chemistry presented here has great potential for on demand reversible bonding applications.

Conclusions

A new reversible, fast, and catalyst-free HDA reaction based on CDTE was developed. A novel synthetic approach for isolating functionalized CDTEs, suitable for further chemistry, employing an in situ trapping with Cp strategy, was pioneered. The rDA behavior of the Cp protected CDTE was explored by temperature dependent on-line UV-Vis and NMR spectroscopy, as well as by ESI-MS and high-level ab initio molecular orbital theory calculations. All theoretical and experimental techniques demonstrated the reversibility of the DA reaction and the relatively low rDA temperature. The practical relevance of the new bonding/debonding on demand chemistry was explored in a polymer system by generating a CDTE-based di-linker, which was polymerized with a bis-Cp polymer (i.e., di-functional diene) in a DA-based step-growth polymerization reaction. The AA–BB polymer obtained was demonstrated to undergo reversible polymerization by SEC analysis, pre- and post-in situ trapping of the polymer with DMBD, and high temperature on-line dynamic light scattering as well as NMR spectroscopy. Time resolved on-line UV-Vis measurements revealed rapid CDTE deprotection, polymerization, and depolymerization. None of the three steps required more than 5 min reaction time. Thus, the HDA reaction presented herein is a key innovation in heat triggered, reversible covalent bond-based systems. These results make the CDTE DA system extremely attractive for reversible covalent bond applications.

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Notes and references