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Harnessing entropy to direct the bonding/debonding of polymer systems based on reversible chemistry†

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The widely accepted approach for controlling polymer debonding/rebonding properties in responsive materials has been to purposefully engineer the functional end-groups responsible for monomer dynamic bonding. Here, however, we evidence that the debonding temperature of a polymer can also be tuned by changing the chain length of the polymer building blocks, thus altering the entropy released on debonding. Entropy driven debonding, as governed by building block chain length, is suggested theoretically and realized experimentally for two Diels–Alder polymer systems, each based on a different difunctional diene and a common difunctional dienophile. In each case a significant decrease (as much as 60 °C) in the retro Diels–Alder temperature was observed when the chain length of the difunctional dienophile building block was increased. These results have the potential to fundamentally change the approach utilized to design materials capable of bonding reversibly on demand.

Introduction

In the last decade polymer chemists have dedicated substantial efforts towards designing polymers that contain stimuli-responsive, dynamically bonding functional groups, which allow the material to undergo reversible debonding in the presence of a specific pre-selected trigger, such as heat,[1–7] light,[8–12] or pH.[13–15] These efforts have been primarily motivated by a desire to generate self-healing materials,[2,16–18] as well as printable networks. Incorporating stimuli-responsive dynamic bonds into polymer backbones not only permits the fabrication of highly functional complex materials with well-tuned properties, but also has the potential to render these materials recyclable.[2,18,19]

The applicability of materials possessing reversible linkages is primarily dependent on the conditions under which bond formation and cleavage occur. In particular, bond cleavage tends to be the most energetically demanding of the two processes, and thus much research has been focused on developing polymer systems optimized to debond under conditions desirable for the target application. In this regard, both the reaction kinetics and thermodynamics must be tailored, so that the reaction proceeds within a reasonable time frame and that the desired final extent of debonding at a given temperature is achieved. The kinetics will depend on the chemistry of the reactive groups and also on the external reaction conditions, such as the building block concentration and the presence of various additives. However, it is the thermodynamics that provide a hard limit to the maximum extent of debonding achievable at a given temperature, and tuning the thermodynamics requires optimization of the chemical structures of the reacting species.‡ This, ultimately, is the focus of the current study.

To date, the widely accepted methodology for tuning the debonding point of a material (*i.e.*, thermodynamics) has been to judiciously design/select the dynamically bonding functional groups that end-cap building blocks that are employed for the formation of polymers or crosslinked networks. Interestingly, although the debonding point of polymers has been successfully modified by changing the chemistry of the functional groups (*i.e.*, reaction enthalpy), discrepancies tend to exist in the reported debonding properties (*e.g.*, debonding temperature) for dynamically bonding functional group pairs, such as

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† Electronic supplementary information (ESI) available: Complete synthesis and experimental details, characterization of the DA polymeric systems, calculation methodologies, and supplementary tables and figures. See DOI: 10.1039/c3sc50642h

maleimide–furan.[2,4,19,20] Based on these discrepancies and theoretical modelling, presented herein, we hypothesized that, in addition to the functional group chemistry, the material stiffness and topology, such as chain length and branching, also affect the debonding properties of dynamically bonding materials. In fact, we suggest that the fundamental principle of entropy has been overlooked during the polymer design stage, and can be harnessed through simple alterations to the chain length of the polymer building blocks to tune the debonding temperature.

The thermo-reversibility of reactions, such as Diels–Alder (DA), disulfide, and alkoxyamine chemistries, is the result of competing enthalpic and entropic contributions to the Gibbs free energy of the reaction. Taking DA bond formation as an example, on the one hand the reaction is typically highly exothermic ($\Delta H < 0$) due to the net gain of 2 σ bonds in place of 2 (weaker) π bonds. On the other hand, the reaction is also highly exentropic ($\Delta S < 0$) due to the net conversion of 6 external degrees of freedom to internal modes. At sufficiently low temperatures the enthalpic term is dominant and the overall reaction exergonic ($\Delta G = \Delta H - T\Delta S < 0$); however, as the temperature increases, the entropic contribution increases until it eventually outweighs the enthalpic term and the reaction becomes endergonic ($\Delta G > 0$). The temperature at which this crossover occurs is determined by the relative sizes of the reaction enthalpies and entropies: specifically, $\Delta G = 0$ when $\Delta H = T\Delta S$. Usually, one tunes this temperature by selecting end-group pairs that give rise to different reaction enthalpies. However, we assert that tuning the entropy of a reversibly bonding system can have equally dramatic effects on the debonding temperature. Although a few publications[21,22] have either directly or indirectly noted the effects of polymer/monomer topology/backbone properties on reversibly debonding polymer systems, no one appears to have correctly isolated the entropic component to analyze its effects on debonding. Here, we propose that the influence of entropy on polymer debonding can be well isolated and analyzed by changing the chain length of the monomeric linkers in a polymer while preserving the chemistry of the backbone and reactive end-group pairs and controlling other experimental variables such as concentration (Fig. 1).

In order to demonstrate the legitimacy of our claim we call upon a previously established difunctional dienophile 1,4-phenylenebis(methylene)bis((diethoxyphosphoryl)methanedithioformate) (P-di-linker) because not only has it been shown to undergo reversible DA-based polymerization with the difunctional diene isophorone bis(sorbic carbamate) (IPDI-SA),[23] but P-di-linker can also be employed as a reversible addition-fragmentation chain-transfer (RAFT) agent. Thus, the chain length of the P-di-linker can be varied, providing a convenient and practical strategy for exploiting the entropic effect. Using theoretical calculations and two different experimental techniques we show that the retro DA (rDA) temperature can be decreased by increasing the chain length of the P-di-linker block in two distinct DA-polymers, one based on IPDI-SA and the other based on bis-cyclopentadiene poly(isobornyl acrylate-*co*-*n*-butyl acrylate) (Cp_2-P(iBoA-*n*BA)). The results presented here suggest that for any given reversibly bonding functional group pair, the debonding point can be tuned simply by varying the chain length of one or both of the building blocks associated with the functional groups. This new insight may revolutionize the way in which polymer chemists design reversibly bonding materials, such as self-healing materials.

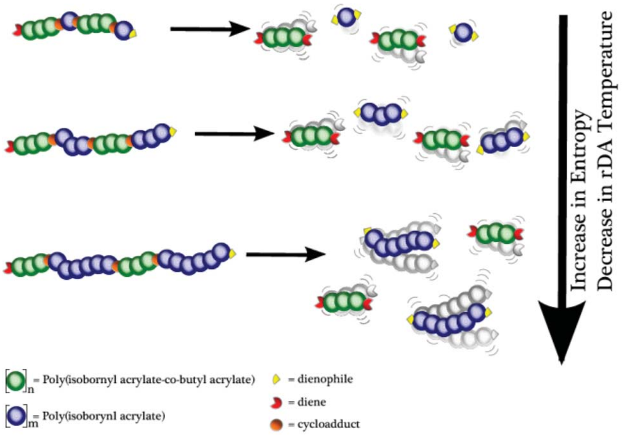
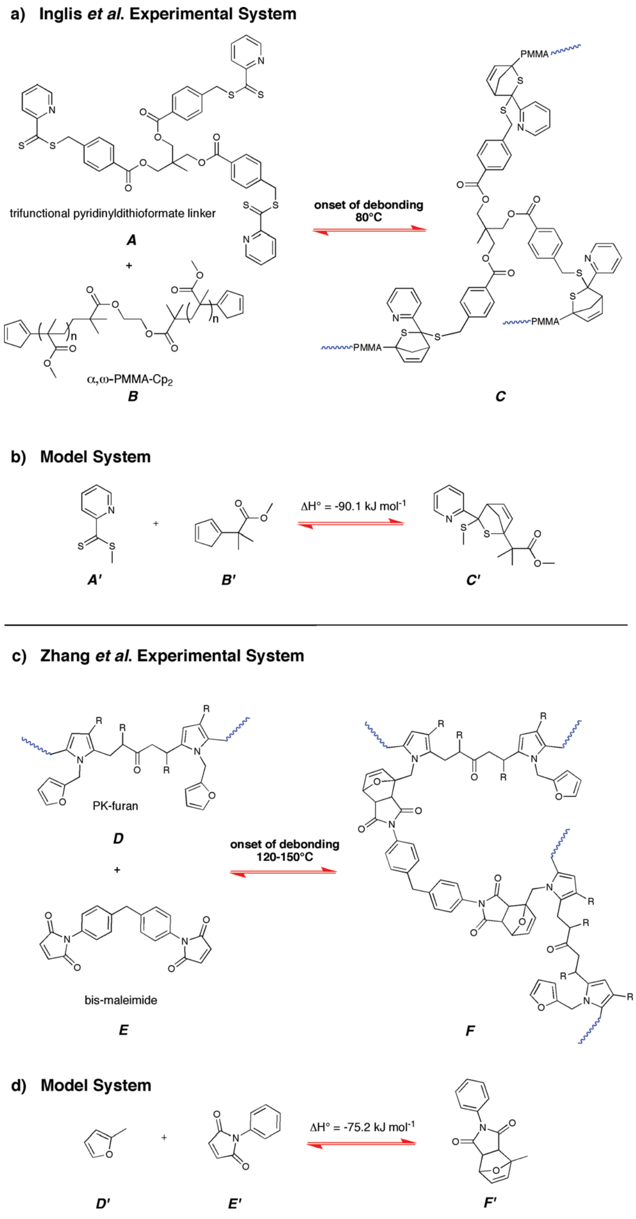


Fig. 1 Schematic representation of the proposed theory stating that more entropy is released as the chain length of a monomer/building block in a polymer is increased. Consequently, a decrease in the debonding temperature should ensue for polymer systems capable of releasing more entropy, since the debonded state is more energetically favorable. Put another way, at any given temperature more debonding will be achieved for systems with the bigger building blocks.

Theoretical predictions

To illustrate the dramatic effects of entropy and enthalpy on the debonding temperature, we first analyze two case studies from literature[1,2] as shown in Scheme 1. The debonding temperatures of these two reactions differ significantly as a result of both the differences in the chemical structures of the Diels–Alder pairs undergoing the *click* reaction, which primarily affects the reaction enthalpy, as well as the variation in the flexibility and topology of the monomeric species and their crosslinked network, which primarily affects the reaction entropy. To tease out these separate enthalpic and entropic contributions to the delinking temperatures, high-level *ab initio* molecular orbital theory calculations have been executed at the G3(MP2) level of theory to obtain enthalpy changes for the corresponding model reactions (Scheme 1), which have been designed to include only the reaction centre and the primary substituents. Any non-conjugated remote substituents were replaced by hydrogen atoms; these deleted substituents can be assumed to have only a minor effect on the reaction enthalpy, though they are expected to have a significant effect on the reaction entropy. The calculated reaction enthalpies for the model reactions can thus be used as a reasonable measure of the corresponding reaction enthalpies for the experimental systems. Using these calculated enthalpies and the experimentally observed delinking temperatures (taken as the point at which $\Delta G = 0$ and assumed to be at the low end of the reported temperature ranges), the



Scheme 1 (a) The experimental reversible crosslinking reaction of Inglis *et al.*[1] and (b) the corresponding small molecule model. (c) The experimental reversible crosslinking reaction of Zhang *et al.*[2] and (d) the corresponding small molecule model.

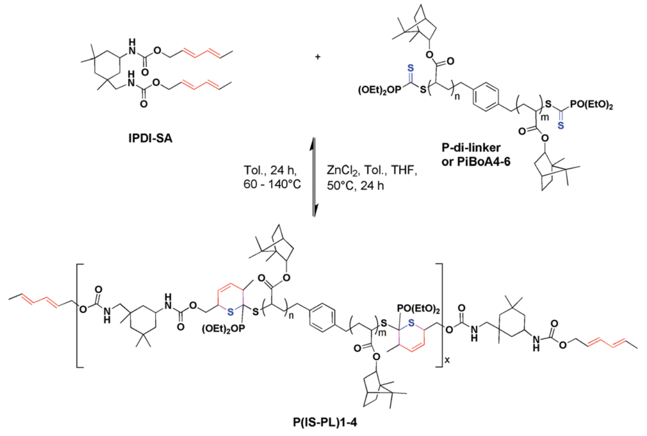
experimental reaction entropies can be estimated by solving $\Delta G = \Delta H - T\Delta S = 0$. In this way, we obtain values of $\Delta S = -255$ J mol^{-1} K^{-1} for the system presented by Inglis *et al.*[1] (Scheme 1a) and -191 J mol^{-1} K^{-1} for the system developed by Zhang *et al.*[2] (Scheme 1c). The calculated reaction entropies of the two experimental systems are significantly different, with the Inglis *et al.* system losing 33% more entropy on reaction than the Zhang *et al.* system. This is likely to result from a complicated interplay between the stiffness of the polymers involved, the density of crosslinks in each case (which is dependent on the conversion), and the molar masses of the starting materials. Based on the results presented here – and on the respective experimental conversions – it would appear that the tri-linked network of Inglis *et al.* is relatively more ordered and rigid following the crosslinking reaction. Or, in other words, relative to the crosslinked network, the debonded network is more disordered due to, for instance, the longer di-linker chain length.

To appreciate the practical significance of these differences in 'experimental' reaction entropies, we can use them in conjunction with the calculated enthalpies to predict the hypothetical effect on the delinking temperature of swapping the chemical structures of the end-groups, whilst all other aspects of the polymeric system (*e.g.*, molecular weight, topology, crosslink density, and conversion) are kept constant. This is a hypothetical situation that may not be practically achievable, yet it serves to illustrate the competing contributions of end-group effects and polymer backbone effects to the delinking temperature. Given the Inglis *et al.* system, if the end-groups (and hence ΔH) were to be kept constant but the general polymeric system (and hence ΔS) was changed to that of Zhang *et al.*, the delinking temperature would change from 80 °C to 198 °C. Alternatively, if the polymer system were to be kept constant and the end groups were to be changed the temperature would change from 80 °C to 22 °C, a change that is significant but surprisingly less dramatic than the effects of entropy.

Normally the polymer type, crosslinking density, and topology are dictated by other practical considerations and are not viable variables for tuning the delinking temperature of a system. However, entropy can still be exploited in a subtler manner through changes to the chain length of the monomeric linking agents. Predicting accurate entropy changes in polymer films from first principles is a very complex task; however, we can often obtain useful *qualitative* insights through illustrative calculations for oligomeric species under ideal gas conditions, for which exact partition functions are available, and in solution, for which reliable free energy changes can be obtained using (semi-empirical) continuum solvation models.

Accordingly, *ab initio* molecular orbital calculations in conjunction with continuum solvation models were utilized to determine the temperature dependent equilibrium constants in toluene solution for the Diels–Alder reaction of the IPDI-SA + P-di-linker DA polymer system (P(IS-PL)) (Scheme 2) with P-di-linkers of various block chain lengths ($n = m = 0$, 1, and 2) (Fig. 2a). We find there is a direct correlation between the size of the P-di-linker and the debonding temperature, which is manifested in the 176 °C decrease in the temperature that is required to achieve 85% debonding when $n = m = 2$ *versus* $n = m = 0$ (Fig. 2b). Consistent with expectation, a more detailed analysis revealed that the enthalpic contribution to the solution phase reaction Gibbs energy is relatively insensitive to chain length and that the decrease in debonding temperature is a direct consequence of entropic and solvation effects (Fig. 2c). There is a steady decrease in the entropy, which is most pronounced in the vibrational component. Inspection of the optimized geometries revealed that the Diels–Alder product adopts folded conformations and this could contribute to more sterically hindered vibrations.

Of course, these small molecule results are likely to differ from those observed for a practical polymeric system. Even the



Scheme 2 DA-based polymerization of IPDI-SA with P-di-linker, PiBoA4, PiBoA5, or PiBoA6 to generate the polymers P(IS-PL)1–4.

solution phase results are only an approximation to the polymer melt, and only likely to be reasonable for building blocks of small chain lengths and at large extents of delinking. However, we expect our qualitative conclusions to be reasonable and, therefore, set out to substantiate these results with experimental studies.

Experimental verification

DA polymerization

Although the theoretical calculations provide insight into the effect of increasing chain length on the debonding temperature of reversibly polymerized building blocks, these results are only qualitative and are limited to polymers composed of very small building blocks. In the interest of validating the theoretical conclusions with experimental evidence and demonstrating the chain length effect over a larger range of building block sizes, the dependence of the rDA properties of two hetero DA (HDA) polymer systems, containing P-di-linker[23] or a P-di-linker-based RAFT polymer, on building block chain length was explored. First, the dual purpose of the P-di-linker (*i.e.*, di-functional dienophile and RAFT agent) was exploited to permit the creation of a library of P-di-linker-derived poly(isobornyl acrylate)s (PiBoAs) (*i.e.*, di-functional dienophiles) of chain lengths corresponding to 6.1, 10.8, 18.9, 20.2, 31.5, and 41.4 kDa, as determined by size exclusion chromatography (SEC) (Table 1). The P-di-linker and each PiBoA was subsequently polymerized with IPDI-SA or Cp_2-P(iBoA-*n*BA) (number average molecular weight (M_n) $\sim$ 13.9 kDa) at 50 °C to generate a library of IPDI-SA + P-di-linker/PiBoA polymers (P(IS-PL)1-4) (Scheme 2) or Cp_2-P(iBoA-*n*BA) + P-di-linker/PiBoA polymers (P(Cp-PL)1-7) (Scheme 3), respectively. Thus, for each library of polymers the chemical composition was the same, yet the P-di-linker-based building block chain lengths varied. Bonding (and later, debonding) percentages were calculated *via* Carother's equation (ESI, Section 3.3.1†) since it correlates M_n values to conversion, which is essentially equivalent to bonding.

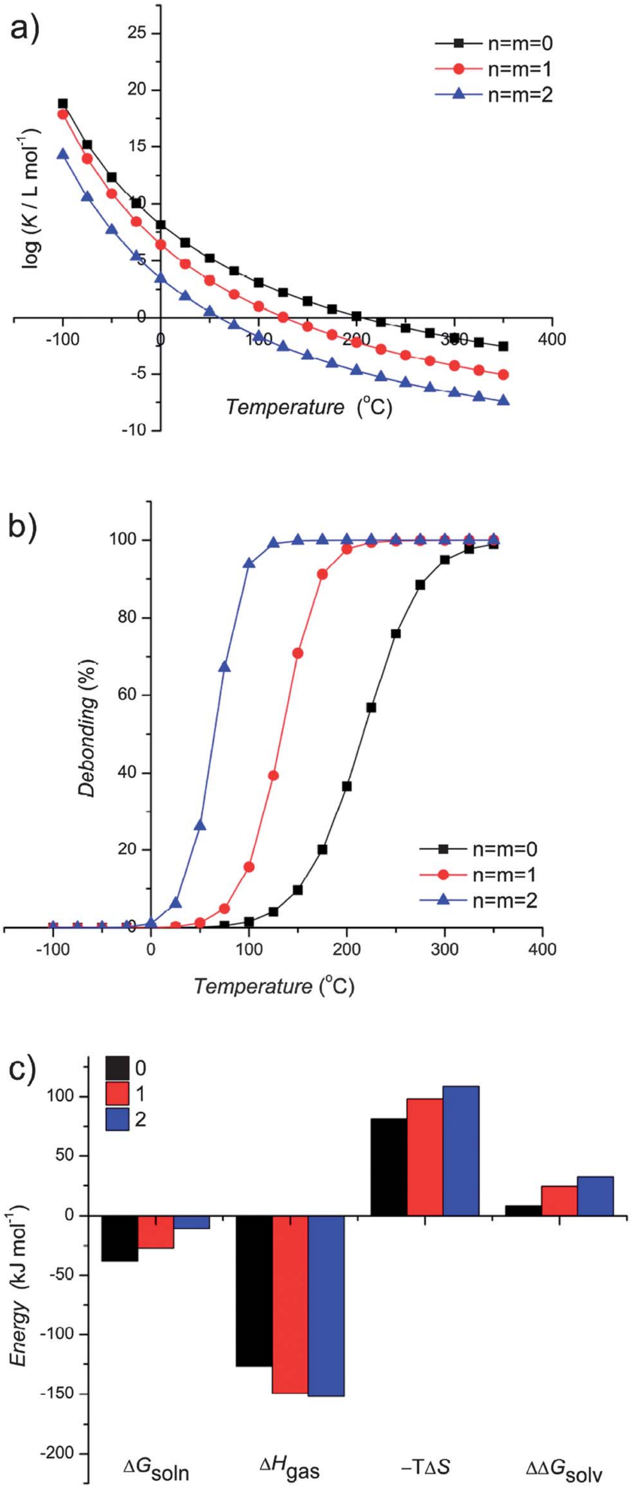
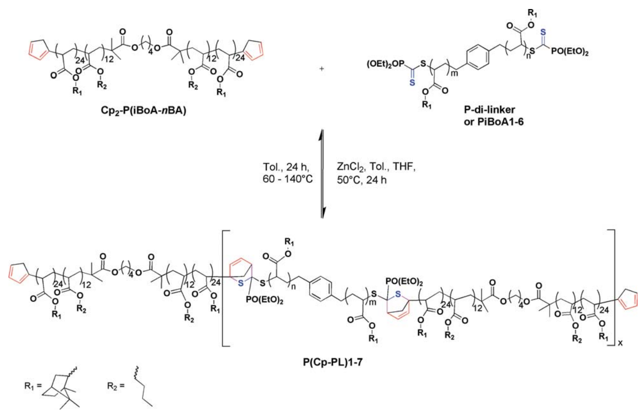


Fig. 2 (a) Graph of temperature *vs.* log *K*, where *K* is the equilibrium constant derived using *ab initio* quantum chemical calculations, for the formation of one cycloaddition reaction in solution for the system shown in Scheme 2. (b) Graph of temperature *vs.* percentage of debonding (determined from *K*). In other words, the temperature corresponds to the retro Diels–Alder temperature necessary to achieve the percentage debonding displayed on the *y*-axis. (c) The gas phase enthalpic, entropic, and solvation contribution to the solution phase reaction energy (ΔG_{soln}) in kJ mol^{-1}. For all panels 0, 1, and 2 refer to the *n* = *m* values.

Table 1 The M_n and bonding percentage values corresponding to the P(IS-PL) and P(Cp-PL) DA polymers derived from IPDI-SA and Cp_2-P(iBoA-*n*BA), respectively. M_n values were determined with respect to poly(methyl methacrylate) standards and PiBoA Mark–Houwink constants

DA Polymer	Dienophile	Dienophile M_n (kDa)	DA Polymer M_n (kDa)	Bonding[a] (%)
P(IS-PL)1	P-di-linker	0.5306	4.5	89
P(IS-PL)2	PiBoA4	20.2	18.7	37
P(IS-PL)3	PiBoA5	31.5	35.8	46
P(IS-PL)4	PiBoA6	41.4	86.8	64
P(Cp-PL)1	P-di-linker	0.5306	28.5	72
P(Cp-PL)2	PiBoA1	6.1	27.7	64
P(Cp-PL)3	PiBoA2	10.8	40.3	69
P(Cp-PL)4	PiBoA3	18.9	37.9	57
P(Cp-PL)5	PiBoA4	20.2	34.6	51
P(Cp-PL)6	PiBoA5	31.5	47.4	52
P(Cp-PL)7	PiBoA6	41.4	51.3	42

[a] See supplementary information for calculation methodology.†



Scheme 3 DA-based polymerization of Cp_2-P(iBoA-*n*BA) with P-di-linker/PiBoA to generate P(Cp-PL)1-7.

Offline SEC characterization of the P(Cp-PL) system

With the DA products in hand, we explored the effect of building block chain length and, therefore, entropy on debonding. Initially, a more traditional experimental protocol was conducted, consisting of the isolation and SEC characterization of the rDA products obtained from P(Cp-PL)1-6 after heating at 60, 80, 100, 120, or 140 °C for 24 h (Fig. 3a). It is important to stress that all rDA reactions were performed under the same molar concentrations with minimal differences in building block molar concentrations, according to the conversion (*i.e.*, % bonding) of the starting materials. The 'decrease in debonding' values, which are plotted as a function of building block chain length in Fig. 3b, were calculated *via* Carother's equation from the M_n of the rDA products and those of the corresponding DA precursors (ESI, Section 3.3.1†).

Fig. 3b reveals that the experimental results corroborate the theoretical predictions. At 60, 80, and 100 °C, the trend is clear: as the P-di-linker-based block size (*i.e.*, dienophile M_n) in the P(Cp-PL) DA polymer is increased, the extent of P(Cp-PL) debonding (relative to the initial bonding present in the DA starting material – Table 1) increases. At high temperatures the apparent chain length effect is minimal because the entropic driving force is so dominant that every system achieves complete debonding. The debonding values over 100% are likely due to the precision limits associated with SEC instruments and the instability of the polymer at temperatures above 120 °C. However, the impact of these results is that the rDA temperature of P(Cp-PL) can be reduced by half, from 120 °C to 60 °C, while still achieving a 50% decrease in debonding, simply by increasing the dienophile block size from 0.5 kDa to 8–9 kDa.

Whilst it is thus clear that the temperature can be increased to a point (here >120 °C) at which all DA polymers, regardless of building block size, achieve 100% debonding, for many applications there are high temperature limitations. Consequently, raising the temperature to achieve a desired level of debonding would clearly not be a realistic option in most practical applications. However, our results show that this limitation could be overcome by increasing the building block size, which in turn can be achieved easily through controlled/living polymerization techniques.

To ensure the reliability of the aforementioned results the experimental protocol was carefully optimized and appropriate controls and bonding values were compared. All rDA reactions were performed at the same low concentration and for an extended period of time (>20 h) to make certain that the rDA reaction went to completion and that the DA reaction (*i.e.*, repolymerization) was minimized. A 20–24 h reaction time was selected because it was well in excess of the 10 h or less required to achieve equilibrium in our rDA kinetic study (ESI, Fig. S13 and S14†). Additionally, following the reaction, care was taken to prevent repolymerization of the rDA products by snap freezing the solution (Fig. 3a). Given the measures taken, we hoped to be observing the final thermodynamic state of each polymer system at a given temperature. Finally, the bonding percentage of the rDA product (which, as mentioned earlier, is necessary for determining the 'decrease in bonding') was calculated from the average building block M_n value derived from the M_n values of the corresponding building block controls (*i.e.*, the building blocks individually subjected to the same exact conditions as employed for the rDA reaction) (Fig. 3a). Subjecting the building blocks to the same high temperature as that employed for the rDA reaction should guarantee that any temperature effects on building block stability or folding are taken into account when the DP_n and, subsequently the bonding percentage, is calculated (refer to ESI, Section 7.3.2 for more information†).

Online temperature dependent SEC characterization of the P(IS-PL) system

Although we took every precaution to ensure that the results obtained utilizing the *offline* SEC are reliable, one potential concern with the *offline* approach is the fact that the DA/rDA equilibrium point, which shifts with temperature, is not being observed 'live'. To address this concern, a high temperature SEC (HT SEC) instrument was utilized in temperature dependent mode to assess the extent of bonding/debonding of the DA

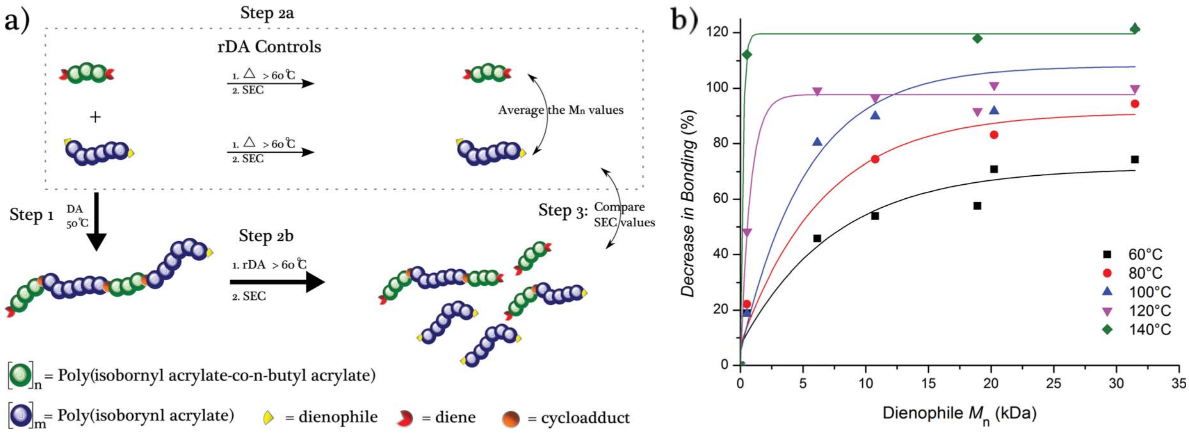


Fig. 3 *Offline* SEC characterization of the rDA properties of the P(Cp-PL) system. (a) Schematic representation of the experimental methodology. Step 1 is the DA synthesis of the polymer from the building blocks (*i.e.*, P-di-linker/PiBoA and Cp_2-P(iBoA-*n*BA)). Step 2 is to heat the DA product and the building blocks separately, but on the same day, at the desired rDA temperature. This step consists of 5 sub-steps: (i) heat a dilute solution of the DA product (or building block) in a pressure tube at the desired temperature for 24 h, (ii) snap freeze the pressure tube in liquid nitrogen, (iii) dilute an aliquot of the reaction mixture, (iv) dry the diluted aliquot for 30–45 min under high vacuum, and (v) immediately analyze the product by *offline* SEC. Step 3 is to average the SEC M_n values of the building blocks and compare that value to the SEC M_n value of the rDA product to get the DP_n from which bonding percentage is calculated. (b) Decrease in bonding *vs.* dienophile (*i.e.*, P-di-linker/PiBoA) M_n at 60, 80, 100, 120, and 140 °C. The >100% debonding values associated with the 140 °C experiment are believed to result from the imprecision of SEC and/or sample decomposition. Consequently, these values are assumed to correlate to 100% debonding. Note, the data points corresponding to the 31.5 kDa building block overlap each other for the 100 °C and 140 °C experiments.

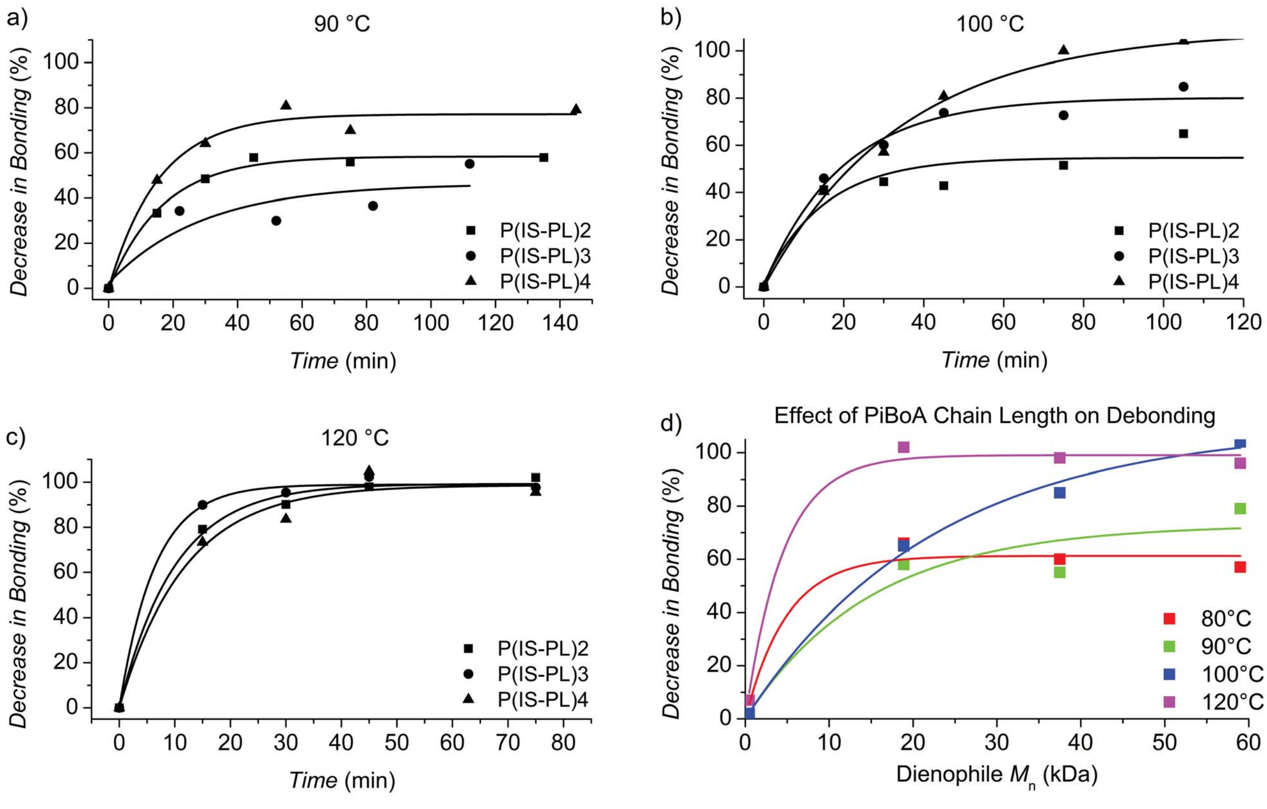


Fig. 4 High temperature *online* SEC kinetic analysis of the rDA reaction of the P(IS-PL) system at (a) 90 °C; (b) 100 °C; (c) 120 °C. (d) Compiled data of the decrease in bonding achieved with respect to dienophile (*i.e.*, P-di-linker/PiBoA) M_n used in the P(IS-PL) for reaction times at equilibrium at 80, 90, 100, and 120 °C. The dienophile M_n values plotted on the *x*-axis correspond to values obtained by light scattering at room temperature (ESI, Section 8.1†).

polymers as the rDA reaction was occurring (*i.e.*, live) at a desired temperature and time. The *online* HT SEC system is similar to the standard SEC system, except that it requires a high boiling point solvent and the autosampler, injection loop, columns, and detectors are all maintained at the desired elevated temperature. The advantage of the HT SEC is that the

DA polymer can be maintained at any temperature (below the boiling point of the solvent) for any given time prior to injecting it into the column. Therefore, the effect of time and temperature on the rDA reaction is observed directly. Although there is evidence that suggests that rDA reactions can be observed by HT SEC,[24] to the best of our knowledge, we are the first to employ HT SEC to perform a detailed evaluation of the rDA reaction of a DA polymer *online* and at different temperatures.

A small subset of the library of P(IS-PL) DA polymers and P(Cp-PL) DA polymers were characterized *online* by HT SEC. Given that such a technique simplified the performance of kinetic studies, the kinetics of the rDA reaction for each DA polymer was characterized at all temperatures. First, it should be noted that the rDA reactions reach equilibrium much more rapidly in small vials in the autosampler than in the pressure tube, which is likely due to the more dilute and smaller volume of DA polymer solution. More significantly, the entropic effect observed previously is observed again for both the P(IS-PL) and P(Cp-PL) systems, with larger chains (*i.e.*, dienophile blocks) resulting in more rapid and greater debonding (Fig. 4d and 5a). Specifically, at temperatures below 120 °C the extent of the rDA reaction of P(IS-PL) (*i.e.*, IPDI-SA-based polymers) proves to be greatly influenced by the building block chain length. For instance, at 100 °C the extent of debonding can be nearly doubled (from ~60% to 100%) by increasing the size of the PiBoA block from ~20 kDa to ~60 kDa. Alternatively, the results indicate that if the dienophile block size is increased from ~20 kDa to ~60 kDa, the rDA temperature can be reduced from ~120 °C to 100 °C while still achieving a 100% decrease in bonding.

The effect of building block chain length and, thus, entropy was found to be similar, although less pronounced, in the P(Cp-PL) system as analyzed by HT SEC. At all temperatures analyzed, (*i.e.*, 80, 100, and 110 °C) there was about a 10% increase in debonding (as represented by a 10% increase in the Cp_2-P(iBoA-*n*BA) content) when the PiBoA block size was increased from ~20 kDa to ~60 kDa (Fig. 5a). The more obvious effects of chain length on debonding are expected to occur for smaller building block sizes, as observed in the *offline* experimental study. However, due to limitations in the data analysis technique the effects of smaller PiBoA block size on polymer debonding could not be characterized *online* (see ESI†). Regardless, the results from both the *online* and *offline* experimental evaluations prove, two times over, that the rDA temperature can be reduced for a given polymer system if the size of the building blocks being released is increased. If we reanalyze all of the *offline* and *online* P(Cp-PL) data in terms of the change in bonding achieved as the chain length increases (Fig. 5b) it is clear that regardless of the temperature there is always an increase (as the change is positive) in debonding as the building block size is increased. Additionally, the chain length effect is greatest for the smaller building block chain lengths.

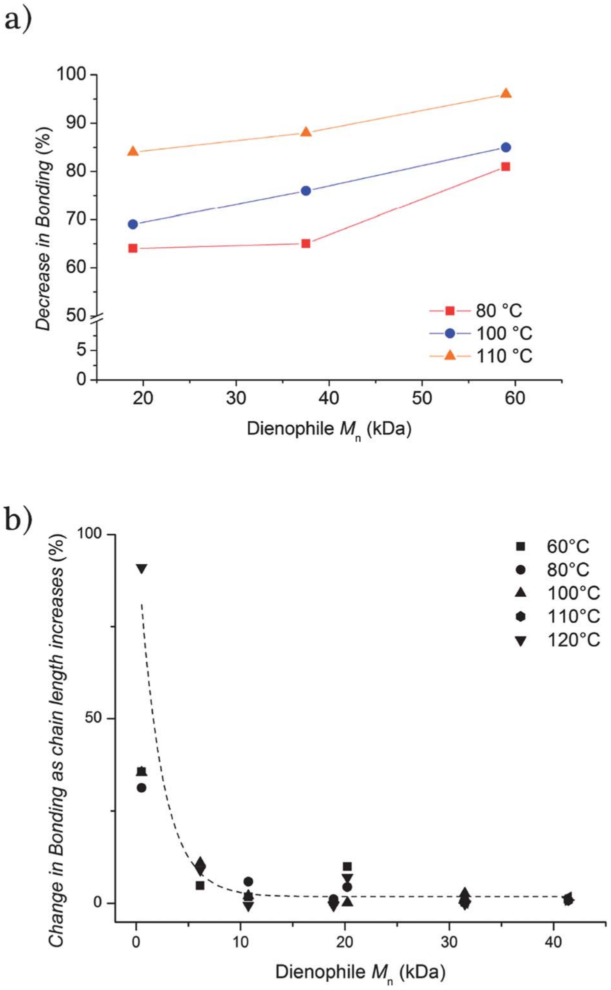


Fig. 5 (a) The decrease in bonding, as assessed by HT SEC, achieved for the rDA reaction of the P(Cp-PL) system based on three different dienophile (*i.e.*, PiBoA) block sizes after 300 min (after equilibrium is reached) at 80, 100, and 110 °C. The decrease in bonding has been calculated according to peak deconvolution methods. Refer to the ESI, Section 3.4.2.† (b) The first derivative of all data points obtained from the *offline* and *online* evaluation of the effect of chain length on the debonding of the P(Cp-PL) DA polymer system. The graph depicts that, regardless of the temperature, as the chain length is increased we always see a decrease in bonding and that this effect is most prominent for changes made to smaller size building blocks.

DA polymer stability

In parallel with completing the rDA studies, the stability of the DA polymers was assessed. Thermal gravimetric analysis (TGA) was employed to verify that changes in the DA polymer M_n value following heating were not due to degradation of the polymers or the building blocks. The monomers and polymers were all found to be adequately thermally stable below 140 °C (ESI, Fig. S4–S6†). In addition, a high temperature, time dependent NMR study was performed in which the P(IS-PL)1 DA polymer was heated to 120 °C and both ^{1}H NMR and ^{31}P NMR spectra were collected continuously for 276 min. These spectra (ESI, Fig. S7 and S8†) demonstrate that at 120 °C the polymer undergoes the rDA reaction to regenerate the IPDI-SA diene and the P-di-linker dithioester. The combined results from the TGA and NMR studies provide evidence that a change in M_n after an rDA reaction can be attributed to debonding and not degradation of the DA polymer.

Conclusions

The work presented here has the potential to transform the approach that polymer and material chemists take to design reversibly/dynamically bonding materials. Currently, the method for tuning the debonding point of dynamically bonding materials has been to purposefully design the reversibly bonding functional groups (*i.e.*, the chemistry), which essentially requires new monomers to be synthesized each time an adjustment of the debonding point is desired. However, in an industrial setting it would likely be more pragmatic and save time, effort, and money if the dynamically bonding functional groups could be maintained and instead the polymer backbone could be altered, which is facilitated by the well-understood controlled/living polymerization techniques available to polymer chemists. In the present work we draw upon a combination of model theoretical calculations and experimental analysis to demonstrate that this is indeed possible in two practical DA-based polymeric systems. In our exploration of the chain length effects on debonding we discover that at temperatures as low as 80 °C nearly an 80% difference in the percentage of debonding of the P(Cp-PL) DA polymer could be obtained if one of the longest building blocks (PiBoA5, $M_n = 31.8$ kDa) was employed compared to the shortest (0.5 kDa) building block (P-di-linker). We suggest that our discovery is just the tip of the iceberg and that much more remains to be explored to fully understand how the polymer topology, and thus entropy, can be harnessed to regulate the debonding properties of materials employed for applications, such as self-healing, shape-memory, and drug delivery.

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Notes and references

‡ In fact, the equilibrium extent of debonding at a given temperature depends not only on the equilibrium constant of the reaction (K) but also very weakly on the starting concentration of reactive end groups (see eqn (7) of ref. 23). In the present work we have controlled for concentration to the best of our ability in all of our experiments so as to isolate the effect of chain length on K. It is worth noting that in a practical bulk polymer system changes to the chain length of a building block (while keeping polymer M_n the same) imply simultaneous changes to the molar concentration of the reactive end groups, and these changes would reinforce the entropy-driven effects of chain length on K itself. We also note that for practical bulk applications tuning K, rather than merely altering the concentration by simple dilution of the dynamically bonding polymers with inactive polymers, is desirable so that the entire material is responsive to temperature.

1 A. J. Inglis, L. Nebhani, O. Altintas and C. Barner-Kowollik, *Macromolecules*, 2010, **43**, 5515–5520.

2 Y. Zhang, A. A. Broekhuis and F. Picchioni, *Macromolecules*, 2009, **42**, 1906–1912.

3 P. Reutenauer, E. Buhler, P. J. Boul, S. J. Candau and J.-M. Lehn, *Chem.–Eur. J.*, 2009, **15**, 1893–1900.

4 X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran and F. Wudl, *Science*, 2002, **295**, 1698.

5 H. Otsuka, K. Aotani, Y. Higaki, Y. Amamoto and A. Takahara, *Macromolecules*, 2007, **40**, 1429–1434.

6 J. Canadell, H. Goossens and B. Klumperman, *Macromolecules*, 2011, **44**, 2536–2541.

7 J. A. Syrett, G. Mantovani, W. R. S. Barton, D. Price and D. M. Haddleton, *Polym. Chem.*, 2010, **1**, 102–106.

8 M. Burnworth, L. Tang, J. R. Kumpfer, A. J. Duncan, F. L. Beyer, G. L. Fiore, S. J. Rowan and C. Weder, *Nature*, 2011, **472**, 334–338.

9 Y. Amamoto, J. Kamada, H. Otsuka, A. Takahara and K. Matyjaszewski, *Angew. Chem.*, 2011, **123**, 1698–1701.

10 S. R. Trenor, A. R. Shultz, B. J. Love and T. E. Long, *Chem. Rev.*, 2004, **104**, 3059–3078.

11 B. Ghosh and M. W. Urban, *Science*, 2009, **323**, 1458–1460.

12 T. F. Scott, A. D. Schneider, W. D. Cook and C. N. Bowman, *Science*, 2005, **308**, 1615–1617.

13 N. Holten-Andersen, M. J. Harrington, H. Birkedal, B. P. Lee, P. B. Messersmith, K. Y. C. Lee and J. H. Waite, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 2651–2655.

14 J. I. Jay, K. Langheinrich, M. C. Hanson, A. Mahalingam and P. F. Kiser, *Soft Matter*, 2011, **7**, 5826–5835.

15 G. Deng, C. Tang, F. Li, H. Jiang and Y. Chen, *Macromolecules*, 2010, **43**, 1191–1194.

16 J. A. Syrett, C. R. Becer and D. M. Haddleton, *Polym. Chem.*, 2010, **1**, 978–987.

17 J. L. Mynar and T. Aida, *Nature*, 2008, **451**, 895–896.

18 P. Cordier, F. Tournilhac, C. Soulié-Ziakovic and L. Leibler, *Nature*, 2008, **451**, 977–980.

19 M. Watanabe and N. Yoshie, *Polymer*, 2006, **47**, 4946–4952.

20 T. A. Plaisted and S. Nemat-Nasser, *Acta Mater.*, 2007, **55**, 5684–5696.

21 K. C. Koehler, A. Durackova, C. J. Kloxin and C. N. Bowman, *AIChE J.*, 2012, **58**, 3545–3552.

22 C. Toncelli, D. C. De Reus, F. Picchioni and A. A. Broekhuis, *Macromol. Chem. Phys.*, 2012, **213**, 157–165.

23 J. Zhou, N. K. Guimard, A. J. Inglis, M. Namazian, C. Y. Lin, M. L. Coote, E. Spyrou, S. Hilf, F. G. Schmidt and C. Barner-Kowollik, *Polym. Chem.*, 2012, **3**, 628–639.

24 E. Espinosa, M. Glassner, C. Boisson, C. Barner-Kowollik and F. D'Agosto, *Macromol. Rapid Commun.*, 2011, **32**, 1447–1453.