Substituent effect on the thermophysical properties and thermal dissociation behaviour of 9-substituted anthracene derivatives

Joost Brancart* a Jonas Van Damme* Filip Du Prez b and Guy Van Assche a

The chemical structure and location of substituents on anthracene derivatives influence the electron balance of the aromatic system, thus determining the wavelengths at which light is absorbed, which results in the photochemically induced dimerization or monomerization. Here, the thermal dissociation kinetics of 7 photodimers of 9-substituted anthracene derivatives are studied using a combination of spectroscopic and calorimetric techniques in the condensed state and compared to scarce literature data on thermal dissociation of other anthracene derivatives. The length and chemical structure of the substituent chains have a clear impact on the melting temperatures of the anthracene derivatives and corresponding photodimers. The crystallinity of the photodimers and monomers in turn influences the thermal dissociation kinetics. The thermal dissociation behaviour and previously published photochemistry data are related to the electronic effects of the substituents by means of the Hammett parameters. Stronger electron-withdrawing effects result in larger red shifts of the maximum wavelength \( \lambda_{\text{max}} \) for the photodimerization of the anthracene derivatives. It is also shown that for the studied substitutions on the 9-position of anthracene, the higher the magnitude of the electronic effect - both electron-donating and electron-withdrawing - the faster the thermal dissociation kinetics and thus the lower the thermal stability. The strong electronic effects of the substituents on the thermal and photochemical reactivity of the anthracene derivatives and their photodimers allow tuning of the thermal or photochemical responsiveness, e.g. for polymer networks.

Introduction

In polymer science, reversible conformational changes have been induced by light irradiation using functional groups such as azobenzenes and spiropyran [1], and for reversible bonding and reversible network formation using, e.g., anthracene [2,3] or coumarin [4] photodimerization. The number of scientific publications on the synthesis of anthracene derivatives, with different substituent chemistries and locations, and the use of their corresponding photodimers as photoresponsive linkers in linear and network polymers is rapidly expanding. Substitution on the 9-position [5–24] and 9,10-disubstitution [3,19,25,26] of the anthracene molecule are most prominent in literature, while also 2-monosubstitutions [27] and 2,6-disubstitutions [28,29] have been documented. The thermophysical and photochemical properties of a great number of anthracene derivatives have been studied, especially after the 1950’s [2,3].

Recently, the photoreversible dimerization reaction of anthracene derivatives became of great interest to organic chemists and material scientists in the scope of various applications and industrial synthesis processes [30]. The photoreversibility of the anthracene dimerization and the feasibility of combining photodimerization and thermal dissociation introduce opportunities for a tuneable (multi-)stimuli-responsiveness of the network properties and dissolution behaviour [8-10,21–23,31].

Most literature focuses on the photodimerization of anthracene derivatives, of which only a fraction also investigates the photodissociation quantitatively and almost exclusively in solution. Calorimetric studies have been performed in the condensed state, reporting melting temperatures of anthracene derivatives and their corresponding photodimers and heats of reaction for the thermal dissociation of, a.o., 9-CHO [5], 9-CN [5,6,25], 9-Me [17], 9-CH2OH [21] and 9-epoxy [22] substituted anthracene derivatives, yet only few document kinetic information on the thermal dissociation of the anthracene photodimers [6,25,32]. The thermal dissociation of anthracene photodimers into anthracene monomers (Equation 1) follows first order reactions kinetics [25,32] with rate constant \( k_{\text{dis}} \) following an Arrhenius behaviour, with \( A_{\text{dis}} \) the pre-exponential factor and \( E_{\text{dis}} \) the activation energy.

\[
D \rightarrow \Delta A \quad \frac{d[D]}{dt} = -k_{\text{dis}}[D] \quad \text{with} \quad k_{\text{dis}} = A_{\text{dis}}e^{-\frac{E_{\text{dis}}}{RT}} \tag{1}
\]

Table 1 summarizes values for corresponding kinetic and thermodynamic parameters found in literature for various anthracene derivatives [3,7]. Most kinetic studies were performed in solution [3,7,19,33]. Ebeid et al. attributed the strong influence of the solvent on the activation energy,
In this work, this methodology has been adapted and applied to study a broad range of anthracene derivatives, for which the photoresponsive properties and thermal dissociation have previously been studied in solution [7]. From the comparison of the thermal dissociation behaviour of the different photodimers in the previous study, several conclusions were drawn. First, it was noted that two photodimers with the same substituent chemistry, but different substituent chain length, showed distinctly different melting temperatures, while their thermal dissociation behaviour in solution was similar due to their similar substituent chemistry and the absence of crystallinity in solution. Other substituents shifted the onset of thermal dissociation by as much as 70 °C. No straightforward link was made between the electronic and inductive effects of the substituents and the activation energies for their respective thermal dissociation behaviour. In this work, newly derived kinetic parameters for a range of anthracene derivatives are compared with existing literature reports and kinetic evaluations performed in solution, with the aim to link the substituent chemistry to the thermophysical properties and thermal dissociation kinetics.

### Experimental

#### Materials
In previous work, 9-substituted anthracene derivatives and corresponding dimers were synthesized to manipulate the electronic substituent effects and their subsequent photoreversible dimerization behaviour [7]. Here, six anthracene derivatives and their photodimers with distinctly different thermophysical and physicochemical properties were selected and studied. The structures of the anthracene derivatives are shown in Figure 1. The synthetic routes to obtain the anthracene derivatives are described in previous work [7,34]. The photodimers were synthesized by irradiation of the various monomer solutions using UV-light at 365 nm, using a mercury arc lamp, resulting in yields over 90% for all anthracene derivatives. In addition to the selected anthracene monomers and dimers, unsubstituted anthracene (A0) and the methanol-substituted anthracene precursor (A7) were evaluated for reference.

Techniques

Fourier Transform Infrared (FTIR) spectra were recorded in transmission mode, inside a heated Perkin Elmer 1700X TG-IR chamber, adapted and fitted to a Nicolet 6700 FT-IR spectrometer from Thermo Fischer Scientific. The crystalline photodimer materials were ground, mixed with KBr powder, and pressed to produce homogeneous pellets for transmission IR spectrometry. The FTIR spectra were recorded with automatic atmospheric suppression using a KBr blank as the background.

Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments Q2000 DSC equipped with a refrigerated cooling system (RCS). Quasi-isothermal DSC experiments were performed with heating and cooling rates of 5 to 20 K min\(^{-1}\) and intermittent short isothermal segments at elevated temperatures per heat-cool cycle. The DSC was purged with a 25 ml min\(^{-1}\) nitrogen purge flow. The Tzero type DSC instrument was calibrated using sapphire discs according to the manufacturer’s instructions. All measurements were performed in aluminium Tzero crucibles using non-hermetic Tzero lids, both acquired from TA Instruments. Enthalpy and temperature calibrations were performed using indium as a calibration standard.

Photocalorimetry (PhotoDSC) experiments were performed on a TA Instruments Q2000 DSC equipped with a photocalorimeter accessory (PCA, TA Instruments). The PCA facilitates irradiation of sample and reference with UV light from a Lumen Dynamics 100 W mercury arc lamp, equipped with a 320–500 nm broad band gap filter. The quartz light guides were fitted with 1% neutral-density 2.0 filters. The relative positions of the light guides with respect to the sample and reference platforms were adjusted to irradiate both sides with approximately the same light intensity. The cell was purged with a nitrogen gas flow of 50 ml min\(^{-1}\). The PhotoDSC was calibrated for 40 µl aluminium crucibles from Mettler Toledo (used without lids), using sapphire (Tzero calibration) and indium (temperature and enthalpy).

Rapid Heat-Cool Calorimetry (RHC) is a prototype technique developed by TA Instruments that enables faster heating and cooling than conventional calorimetric techniques due to smaller furnace, pan, and sample sizes (100–500 µg instead of several mg) and by radiative heating of the RHC cell using four quartz halogen lamps. Calibrations were performed following the procedure described in [35]. The RHC was equipped with a liquid nitrogen cooling system (LNCS) and the cell was purged with a 10 ml min\(^{-1}\) helium purge flow. Dedicated aluminium sample crucibles and lids from TA Instruments were used [35].

Results and discussion

Thermophysical properties

The thermophysical properties of the photodimers of the different anthracene derivatives were studied using calorimetric techniques. As is typically reported for anthracene and its derivatives [36,37], the anthracene dimers and monomers studied in this work are crystalline at room temperature. According to literature, the melting temperature of the photodimer of unsubstituted anthracene is about 355 °C (predicted using the Joback method [38]). Rapid Heat-Cool Calorimetry (RHC) results confirmed melting at temperatures above 320 °C at a heating rate of 1000 K min\(^{-1}\) (Figure 2, D0, solid line), in an attempt to determine the melting temperature without significant thermal dissociation or degradation. At these elevated temperatures, the photodimer quickly dissociates into anthracene monomer and evaporates from the RHC crucible. Heat-cool cycles in DSC until 250 °C show gradual build-up of the melting peak of the anthracene monomer formed by thermal dissociation (first dashed, then dotted lines), even at temperatures well below the melting temperature of the photodimer.

The dimers studied in this work show distinctly different melting and crystallization behaviour (Figure 2, solid lines). The melting trajectories can easily be identified as the endothermic (positive) peaks in the DSC curves. The melting temperatures of the dimers strongly depend on the chemistry and the length of the substituents. The D7 photodimer of 9-anthracenemethanol (A7 in Figure 1), which is substituted with a hydroxymethyl group and serves as a starting product to synthesize A5 and its...

Figure 1 Structures of the anthracene derivatives (An) and of the head-to-tail and head-to-head stereoisomers of D2, the photodimer of monomer A2. All dimers are formed via a [4 + 4] photocycloaddition.

This journal is © The Royal Society of Chemistry 20xx J. Name., 2013, 00, 1-3 | 3
photodimer D5, has the highest melting temperature ($T_m > 200^\circ C$) of the studied photodimers, reflecting the lowest impact on the crystallization and melting behaviour of dianthracene D0. Similarly, the high $T_m$ of dimers D6 and D4 is attributed to the short substituent groups of just 3 and 4 atoms long (not including hydrogen atoms), respectively. Dimer D3, with the same substituent chemistry as D4 but having a longer substituent chain (12 carbon atoms), shows a much lower $T_m$, clearly illustrating the effect of the substituent chain length as previously reported [7]. Dimer D5 shows a $T_m$ similar to that of D3, with similar flexibility and length of the substituent chains, whereas the $T_m$ of dimer D2 is higher. The latter dimer has a
Table 2. Thermophysical properties of the synthesized anthracene monomers and their corresponding dimers: the glass transition temperature \( T_g \), the onset temperature of melting \( T_m \) and the melting enthalpy \( \Delta mH \) of dimers and monomers, onset temperature \( T_r \) and reaction enthalpy \( \Delta H \) of the thermal dissociation of the studied dimers.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>( T_g ) (°C)</th>
<th>( T_m ) (°C)</th>
<th>( \Delta mH ) (kJ mol(^{-1}))</th>
<th>Dimer</th>
<th>( T_g ) (°C)</th>
<th>( T_m ) (°C)</th>
<th>( \Delta mH ) (kJ mol(^{-1}))</th>
<th>( T_r ) (°C)</th>
<th>( \Delta H ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>215</td>
<td>27.3</td>
<td>n.d.(^{b})</td>
<td>D0</td>
<td>n.d.(^{b})</td>
<td>&gt; 320(^{d})</td>
<td>n.d.(^{c})</td>
<td>n.d.(^{f})</td>
<td>n.d.(^{f})</td>
</tr>
<tr>
<td>A1</td>
<td>-58</td>
<td>n.a.(^{a})</td>
<td>n.a.(^{a})</td>
<td>D1</td>
<td>-25</td>
<td>84</td>
<td>34.1</td>
<td>150</td>
<td>-18.9</td>
</tr>
<tr>
<td>A2</td>
<td>-54</td>
<td>52</td>
<td>42.3</td>
<td>D2</td>
<td>-8</td>
<td>143</td>
<td>34.5</td>
<td>180</td>
<td>-28.3(^{a})</td>
</tr>
<tr>
<td>A3</td>
<td>-57</td>
<td>11</td>
<td>20.4</td>
<td>D3</td>
<td>-50</td>
<td>107</td>
<td>14.5</td>
<td>135</td>
<td>-24.3</td>
</tr>
<tr>
<td>A4</td>
<td>-51</td>
<td>66</td>
<td>26.1</td>
<td>D4</td>
<td>n.d.(^{b})</td>
<td>187</td>
<td>n.d.(^{b})</td>
<td>n.d.(^{b})</td>
<td>n.d.(^{b})</td>
</tr>
<tr>
<td>A5</td>
<td>-33</td>
<td>61</td>
<td>n.d.(^{a})</td>
<td>D5</td>
<td>15(^{d})</td>
<td>119</td>
<td>25.4(^{b})</td>
<td>n.d.(^{b})</td>
<td>-31.8(^{a})</td>
</tr>
<tr>
<td>A6</td>
<td>26</td>
<td>141</td>
<td>17.5</td>
<td>D6</td>
<td>40(^{b})</td>
<td>&gt; 200(^{d})</td>
<td>21.9(^{b})</td>
<td>165</td>
<td>-15.7(^{a})</td>
</tr>
<tr>
<td>A7</td>
<td>186</td>
<td></td>
<td>n.d.(^{b})</td>
<td>D7</td>
<td>222(^{a})</td>
<td>28.5(^{c})</td>
<td>n.d.(^{b})</td>
<td>n.d.(^{b})</td>
<td>n.d.(^{b})</td>
</tr>
</tbody>
</table>

\(^{a}\) Monomer A1 does not crystallize. Monomer A5 crystallizes very slowly.

\(^{b}\) Due to the high \( T_g \), these properties cannot be determined quantitatively, without considerable thermal dissociation.

\(^{c}\) The thermal properties cannot be determined quantitatively without thermal degradation or evaporation.

\(^{d}\) Measured using RHC at 2000 K min\(^{-1}\) to minimize the thermal dissociation of the dimer after melting.

\(^{e}\) Optimized heats of reaction fitting simulated heat flows from FTIR data with experimental heat flows from DSC.

substituent chain that is similar in length (13 atoms) to that of D3 and D5, but includes a more polar ester group. Dimer D1 has the lowest \( T_m \) of all studied anthracene dimers. In this case, the ester group is directly bonded to the anthracene ring, resulting in a strong electron withdrawing effect, interfering with the crystallization of the aromatic rings and side chains.

Analogous trends are observed for the anthracene monomers (dotted lines), with little or no crystallization observed for monomers A1, A3 and A5. The melting temperature of pure anthracene is established at 215 °C, which is higher than the \( T_m \) of all substituted monomers. The results of the calorimetric evaluation are summarized in Table 2.

At elevated temperatures – usually above the melting temperatures of the dimers – exothermic peaks can be observed for all dimers, originating from their thermal dissociation into the corresponding anthracene monomers. For dimers D1, D2 and D3 the thermal dissociation (monomerization) starts at temperatures well above the melting trajectory (at a heating rate of 10 K min\(^{-1}\)). For dimers D4 and D5, the melting sharply switches to an exothermal dissociation, indicating that the molten dimers quickly dissociate. Conversely, dimer D6 is the melting point above 200 °C and thermal dissociation already occurs before melting is observed, resulting in a complex melting behaviour. Similar results are observed for the methanol-substituted dimer D7 and the unsubstituted dianthracene D0, in line with their high melting temperatures.

Thermal dissociation kinetics study
In previous work [32], a method was set up to accurately study the thermal dissociation kinetics of anthracene photodimers D1 and D2. Structural information from temperature-controlled time-resolved FTIR spectroscopy was combined with the thermophysical information provided by DSC. Above the melting temperature of the dimer, the natural logarithm of the reaction conversion decreased linearly as a function of time, with a slope equal to \(-k_{dis}\), for the monomolecular dissociation of the dimer (Equation 1) at different temperatures. The pre-exponential factor \( A_{dis} \) and the activation energy \( E_{dis} \) were obtained from the Arrhenius plots. For the thermal dissociation at temperatures below the melting temperature, new Arrhenius parameters could be found, showing a clear effect of the crystallinity of the dimer on the reaction kinetics [32]. The reported values are listed in Table 3. In this study, the same method was used to study the thermal dissociation of a wider range of anthracene photodimers to assess the influence of the electronic substituent effect. The temperature-controlled time-resolved FTIR spectroscopy data can be found in Figure SI1. The resulting Arrhenius plots in the crystalline state (empty markers) and in the molten, amorphous state (filled markers) are compared in Figure 3.

Dimers D3 and D4 have the same substituent chemistry, yet distinctly different melting temperatures of 107 °C and 187 °C, respectively, due to the difference in length of the substituent chain of 12 and 4 carbon atoms, respectively. The thermal dissociation behaviour of dimer D3 could be studied above its melting temperature, resulting in a single set of Arrhenius
parameters (filled markers in Figure 3) at these temperatures. For temperatures below the melting temperature, the conversion changes slower as a function of time than if the rate constant at that temperature would follow the same Arrhenius behaviour (Figure SI1), resulting in an additional set of parameters for the thermal dissociation in the crystalline state (empty markers in Figure 3). The thermal dissociation is much slower from the crystalline state, than from the molten state. As the thermal dissociation progresses, more dimer is dissociated into monomer and a melting point depression is observed (Figure 4), similar to what was reported earlier for dimer D1 and D2 [34]. This is reflected by the filled markers at temperatures below the melting temperature. These markers follow the same behaviour as in the molten state. It should be noted that this difference in thermal dissociation behaviour is not present in solution for dimers D3 and D4 (denoted (10)2 and (9)2 respectively in [7]) due to the absence of crystallinity in solution. For dimers D4, D5 and D6 no quantitative thermal dissociation experiments could be performed at temperatures above Tm. For D4 and D5 two sets of parameters could be found below their respective melting temperatures, similar to D2 and D3. First the crystalline dimers dissociate (empty markers in Figure SI1 and Figure 3) into their corresponding monomers, which are in a molten state at those temperatures. At a certain point, the reaction rate speeds up (slopes in Figure SI1), as the remaining dimer is dissolving into the formed monomer. The thermal dissociation from the mixed phase of molten monomer and dimer proceeds faster than for the purely crystalline dimer (filled markers in Figure SI1), resulting in a second set of parameters at these temperatures (filled markers in Figure 3).

Table 3 compares the Arrhenius parameters for all studied dimers in the crystalline and the molten state where applicable.

**Table 3.** Kinetic parameters obtained by FTIR spectroscopy for the thermal dissociation of anthracene dimers: pre-exponential factor $A_{dis}$, activation energy $E_{dis}$, temperature $\Theta_{1h}$, at which the half-life time $t_{1/2}$ equals 1 h, and half-life time $t_{1/2}$ values.

<table>
<thead>
<tr>
<th>Dimers</th>
<th>State</th>
<th>$A_{dis}$ (s⁻¹)</th>
<th>$E_{dis}$ (kJ mol⁻¹)</th>
<th>$\Theta_{1h}$ (°C)</th>
<th>100 °C</th>
<th>120 °C</th>
<th>150 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>Amorphous</td>
<td>9.89 × 10¹²</td>
<td>128.3</td>
<td>127.8</td>
<td>18 h</td>
<td>128 min</td>
<td>8 min</td>
</tr>
<tr>
<td>D2*</td>
<td>Crystalline</td>
<td>5.41 × 10¹⁰</td>
<td>362.8</td>
<td>153.2</td>
<td>249 y</td>
<td>237 d</td>
<td>n.a.*</td>
</tr>
<tr>
<td>D2*</td>
<td>Amorphous</td>
<td>9.61 × 10¹⁰</td>
<td>129.5</td>
<td>157.9</td>
<td>11 d</td>
<td>32 h</td>
<td>118 min</td>
</tr>
<tr>
<td>D3</td>
<td>Crystalline</td>
<td>3.28 × 10⁸</td>
<td>237.3</td>
<td>111.5</td>
<td>10 h</td>
<td>n.a.*</td>
<td>n.a.*</td>
</tr>
<tr>
<td>D3</td>
<td>Amorphous</td>
<td>3.16 × 10⁸</td>
<td>135.8</td>
<td>116.3</td>
<td>6 h</td>
<td>40 min</td>
<td>2 min</td>
</tr>
<tr>
<td>D4</td>
<td>Crystalline</td>
<td>3.58 × 10⁸</td>
<td>228.7</td>
<td>149.4</td>
<td>231 d</td>
<td>5.4 d</td>
<td>55 min</td>
</tr>
<tr>
<td>D4</td>
<td>Amorphous</td>
<td>1.28 × 10⁹</td>
<td>127.3</td>
<td>147.2</td>
<td>4.2 d</td>
<td>12.4 h</td>
<td>47 min</td>
</tr>
<tr>
<td>D5</td>
<td>Crystalline</td>
<td>1.00 × 10¹⁰</td>
<td>165.2</td>
<td>106.8</td>
<td>155 min</td>
<td>10 min</td>
<td>17 s</td>
</tr>
<tr>
<td>D5</td>
<td>Amorphous</td>
<td>6.29 × 10¹⁰</td>
<td>136.2</td>
<td>94.8</td>
<td>33 min</td>
<td>4 min</td>
<td>14 s</td>
</tr>
<tr>
<td>D6</td>
<td>Crystalline</td>
<td>3.96 × 10¹⁶</td>
<td>164.5</td>
<td>149.8</td>
<td>22 d</td>
<td>35 h</td>
<td>59 min</td>
</tr>
<tr>
<td>D6 **</td>
<td>Solution</td>
<td>6.3 × 10¹³</td>
<td>154</td>
<td>186</td>
<td>459 d</td>
<td>37 d</td>
<td>31 h</td>
</tr>
<tr>
<td>(3)²* = D5</td>
<td>Solution</td>
<td>1.74 × 10¹⁷</td>
<td>176</td>
<td>165.5</td>
<td>199 d</td>
<td>267 h</td>
<td>352 min</td>
</tr>
<tr>
<td>(9)²* = D3</td>
<td>Solution</td>
<td>1.32 × 10⁸</td>
<td>87.7</td>
<td>113.9</td>
<td>2.8 h</td>
<td>39 min</td>
<td>5.8 min</td>
</tr>
<tr>
<td>(10)²* = D2</td>
<td>Solution</td>
<td>8.04 × 10⁶</td>
<td>77.8</td>
<td>109.5</td>
<td>1.9 h</td>
<td>31 min</td>
<td>5.8 min</td>
</tr>
<tr>
<td>(14)²* = D1</td>
<td>Solution</td>
<td>1.08 × 10⁹</td>
<td>98.7</td>
<td>131.2</td>
<td>12 h</td>
<td>139 min</td>
<td>16.3 min</td>
</tr>
<tr>
<td>(18)²* = D4</td>
<td>Solution</td>
<td>1.46 × 10⁸</td>
<td>92.0</td>
<td>100.0</td>
<td>1.0 h</td>
<td>13.2 min</td>
<td>1.8 min</td>
</tr>
<tr>
<td>(19)²*</td>
<td>Solution</td>
<td>5.39 × 10⁶</td>
<td>82.6</td>
<td>139.8</td>
<td>13 h</td>
<td>202 min</td>
<td>33.7 min</td>
</tr>
</tbody>
</table>

* Temperature above the melting temperature. A calculation for the crystalline state has no physical meaning.

** Calculations for the unsubstituted anthracene dimer, based on values for $A_{dis}$ and $E_{dis}$ from literature [3]

* Reported by Brancart et al. in the condensed state [32] and by Van Damme et al. in solution [7]
The melting temperature of dimer D6 was so high that the dimer remained crystalline throughout the entire thermal dissociation experiment using temperature-controlled time-resolved FTIR at temperatures close to the limits of the heated chamber. Due to the high melting temperatures and the fast dissociation kinetics at these elevated temperatures, the phase behaviour could not be studied quantitatively for dimers D4, D5, D6, D7 and D0 using DSC, in contrast to the earlier reported (partial) phase diagrams for dimers D1 and D2 [32].

Quasi-isothermal calorimetric experiments have been performed at temperatures below $T_m$, however, no quantitative kinetic data was extracted from these measurements (Figure 4). As anthracene monomer A5 does not crystallize fast enough, the build-up of the $T_g$ of the monomer was observed, along with the decrease of the onset temperature $T_m$ of melting of the dimer. However, without quantitative information about the melting enthalpy, no mole fractions could be determined. The progress for the thermal dissociation of dimers D6, D7 and D0 could be tracked qualitatively following the evolution of the
melting peaks of their respective monomers, however, no conclusive information is present from the start of the reaction.

As demonstrated in previous work [32], the heat flow due to the thermal dissociation of the anthracene photodimers can be simulated accurately using the kinetic parameters obtained from the FTIR spectroscopy evaluations, listed in Table 3. Using the rate parameters and the reaction enthalpy $\Delta_r H$ obtained by DSC, the heat flow $HF(t)$ can be simulated following Equation 2 and compared to the experimental heat flows, as presented in Figure 5 for dimers D1 through D6. For D1, D2, D3 and D5 the kinetic parameters obtained in the molten state describe the reaction exothermicity in the calorimetric experiments very well at temperatures above their respective $T_m$. The heat of reaction for D3 could be determined from the DSC experiment as $-41.9 \text{ J g}^{-1}$ (-24.3 kJ mol$^{-1}$). On the other hand, the heat of reaction for D5 could not be determined quantitatively from the DSC experiment due to overlap of the melting of the dimer and the thermal dissociation reaction. The heat of reaction was optimized to fit the experimental data. The optimized heat of reaction for D5 was $-42 \text{ J g}^{-1}$ (-31.8 kJ mol$^{-1}$).

$$HF(t) = \frac{dx(t)}{dt} \Delta_r H - k_{\text{diss}} x(t) \Delta_r H$$  \hspace{1cm} (2)

The melting temperature of D5 is so high that the melting of the dimer interferes much more with the thermal dissociation, as can be seen by the endothermic melting peak sharply changing into an exothermic reaction peak. The heat flow signal of D4 was simulated using the kinetic parameters from the amorphous state (red dotted lines in Figure 5) and using the parameters from the crystalline state (red dashed lines). Neither of the simulated curves using thermal dissociation reaction kinetic parameters fit the experimental DSC signal, as they do not account for the melting transition and the delayed onset of thermal dissociation due to the crystallinity of the dimers. Just after the melting of D4, the higher stability of the dimer

Figure 5 Thermal dissociation of anthracene photodimers D3 to D6: Experimental (DSC, solid black lines) and simulated (using FTIR data, dotted and dashed red lines) heat flow at 10 K min$^{-1}$. The monomer molecular structures are shown.
molecules in the crystals leads to a higher concentration of remaining undisassociated dimer at these temperatures. An arbitrary heat of reaction is used to visualize the heat flow, as the experimental heat of reaction could not be measured or optimized.

Heating dimer D6 at 10 K min⁻¹ first results in the thermal dissociation of the dimer, starting at temperatures well below its Tm, as can be seen by the exothermic slope of the curve. The heat flow signal simulated based on the kinetic parameters obtained in the crystalline state is in very good agreement with the experimental heat flow. As the total reaction enthalpy ΔH could not be quantitatively determined, it was optimized to fit the experimental heat of reaction. Nevertheless, the shape of the reaction exotherm fits perfectly, up to the point where the dimer starts to melt, resulting in a more complex behaviour. The optimized heat of reaction for D6 was -35.5 J g⁻¹ (or -15.7 kJ mol⁻¹). The thermal dissociation kinetics of dimer D7 could not be studied accurately due to the very high Tm. From Figure 2 it could already be seen that the thermal dissociation behaviour is strongly influenced by the high stability of the dimer crystals, similar to dimer D4 and D6. A clear exothermic reaction peak is overlapping with the melting endotherm, resulting in an apparent splitting of the melting endotherm. Moreover, at these temperatures the anthracene monomers evaporate or thermally degrade, rendering a quantitative study practically impossible.

Relation between substituent chemistry and thermal dissociation

The results for the kinetic evaluations of the thermal dissociation of all anthracene photodimers are presented in Table 3 and compared to literature data in solution [7]. With the exception of D5, all dimers show clearly lower dissociation activation energies in solution (78-99 kJ mol⁻¹) than in the molten (128-136 kJ mol⁻¹) or crystalline (164-363 kJ mol⁻¹) state. For all dimers, the pre-exponential factor is larger in the crystalline state (at least 10¹⁵ s⁻¹) than in the amorphous state (10¹¹-10¹³ s⁻¹) or in solution (below 10¹⁰ s⁻¹, except for D5). The higher pre-exponential factor in the crystalline state corresponds with a larger activation entropy, which agrees with a lower (translational) entropy for dimer molecules in the crystals (compared to the liquid, assuming translational mobility and thus the loss of the crystalline state is already gained in the transition state). This is in agreement with what was earlier reported by by Donati et al. for the thermal dissociation of the photodimers of 9-cyano- and 9-cyano,10-acetoxy-anthracene derivatives below their melting temperatures of 170 and 200 °C, respectively, for which the thermal dissociation was studied at temperature below the melting temperature of both anthracene dimers and monomers [25].

\[ t_{1/2} = \frac{\ln 2}{k_{dis}} = \frac{\ln 2}{A_{dis} e^{-E_{dis} / R T}} \]  
\[ \vartheta = \frac{E_{dis}}{R \ln(\frac{t}{\ln 2 A_{dis}})} \]  

In addition to the pre-exponential factors Adis and activation energies Edis in Table 3, the half-life times t₁/2 (Equation 3) are calculated at different temperatures to aid the comparison of their thermal dissociation kinetics. For the dimers D2, D3, D4 and D5, dissociation kinetics in both the crystalline and amorphous phase could be determined. For D1 and D6, kinetic data are only available for the amorphous and crystalline state, respectively. The half-life times for the crystalline state are tabulated for temperatures below the melting temperatures of the dimers only. The half-life times for all dimers are compared in Figure 6. The thermal dissociation proceeds fastest for the OR-substituted dimer D5, followed by the C2H4N2H2-substituted D3 and 9-COR-substituted D1. It should also be noted that the thermal dissociation for the C2H4NH2-substituted D6 occurs faster from the crystalline state than the C6H4-substituted D4 and CH2OCOR-substituted D2, even in the molten, amorphous state. The transition from the thermal dissociation in the crystalline state to the molten state is shown as an abrupt change in the dissociation kinetics around the melting temperatures. In reality, the transition is less abrupt and at temperatures below Tm, the dissociation first occurs in the crystalline state, followed by a complex phase behaviour. Finally, dissociation occurs from a molten (dissolved) state, as observed in the DSC results in Figure 4, showing the melting point depression of dimer D3 with the progress of the dissociation and previously discussed in more detail for D1 and D2 [32].

The thermal dissociation kinetics can also be compared based on the temperature θ₁h at which the half-life time equals 1 h (Equation 4). These values are listed in Table 3 and shown in Figure 7 with respect to the electronic substituent effects. First, it should be noted that for dimers D2 and D3 θ₁h is lower for the crystalline state than for the molten state. For both dimers, Tm is lower than θ₁h, meaning that at θ₁h, the dimers are in a molten state and values for the crystalline state above their Tm have no physical meaning. The θ₁h value of dimer D4 is 149 °C, which is almost 40 °C below the Tm of the highly stable dimer crystals. This explains the calorimetric behaviour seen in Figure 5, showing an abrupt change from an endothermic melting peak to an exothermic dissociation peak. Due to the large difference between θ₁h and Tm and the higher concentration of undisassociated dimer molecules, the reaction rate is much higher...
substituents on the reactivity, the $\sigma_p$ parameters were calculated using the Hammett equation for the ionization of benzoic acid with para-substituted derivatives [40]. To get more insight how the substituent chemistry influences the thermal dissociation kinetics of the dimers, $\theta_{1h}$ values are related to the substituent constants $\sigma_p$ in Figure 7(a). The unsubstituted anthracene dimer shows the highest $\theta_{1h}$ and thus the slowest reaction kinetics (based on the results obtained in solution by Bouas-Laurent et al. [3]), while $\theta_{1h}$ decreases for increasing magnitudes of the substituent constants, in both the negative and positive direction. This implies that the larger the electron-donating or electron-withdrawing effect of the substituent, the less thermally stable is the dimer.

The maximum absorption wavelengths $\lambda_{\text{max}}$ for the photodimerization of the anthracene monomers, determined in earlier work [7], are plotted as a function of $\sigma_p$ in Figure 7(b). The electronic effect of the substituents was shown to produce a shift in the wavelengths for the photodimerization of the corresponding anthracene derivatives. The stronger the electron donating effect of the substituent, the smaller the energy gap between the HOMO and LUMO and the larger the red shift in $\lambda_{\text{max}}$ (towards higher wavelengths). This is confirmed in Figure 7(b), as $\lambda_{\text{max}}$ decreases with increasing values of $\sigma_p$, with the exception of the unsubstituted anthracene dimer, which has the lowest $\lambda_{\text{max}}$ at $\sigma_p$ equal to zero. In other words, the red shift of $\lambda_{\text{max}}$ increases with an increasingly negative substituent effect. The resonance contributions to $\sigma_p$ are larger than the field effects and inductive contributions, meaning that the strongest electron-donating effects result in the largest red shift, as seen for the ether group in D5.

The different trends for the thermal dissociation behaviour and for the photophysical properties allow for a careful tuning of the thermal stability and photoresponsiveness of the anthracene derivatives in view of intended applications. Figure 7(c) shows for dimers D2, D4, D3 and D5 that as the photoresponses convert the visible light spectrum, with increasing $\lambda_{\text{max}}$, the thermal stability of the dimers decreases with decreasing $\theta_{1h}$, suggesting that photoresponsiveness in the visible light region ($\lambda_{\text{max}}$ around 400 nm) is not attainable in conjunction with sufficient thermal stability ($\theta_{1h}$ well above ambient temperature). Nevertheless, it should be noted that a large red shift has already been achieved with the studied anthracene derivatives, moving $\lambda_{\text{max}}$ towards the more intense part of the solar spectrum. It should also be noted that as the photoresponsiveness is closer to the visible light region and thermal dissociation kinetics increase, a dynamically reversible character of the anthracene dimer bonds may be achieved.

For the thermal dissociation from the solid state of the cyano-substituted anthracene photodimers studied by Donati et al., only activation energies were reported [22]. Furthermore, the dissociation was studied from the crystalline state, given the high melting temperatures of the photodimers and anthracene monomers. With a $\sigma_p$ value of 0.66, higher than any of the anthracene derivatives studied in this work, it is reasonable to
assume that the cyano-substituted anthracene derivatives absorb UV light at lower wavelengths than the derivatives studied in this work (Figure 7(b)) and that their corresponding photodimers are less thermally stable (Figure 7(a)). This is supported by the low temperatures observed for the exothermicity of the thermal dissociation, even in the crystalline state and their observation that the 9-CN,10-Ac-substituted photodimer slowly dissociated in the dark at room temperature. After 343 hours (14 days), no trace of the photodimer could be found using calorimetry.

Thermal and photochemical reversibility

The reversibility of the thermal dissociation and the photodimerization of the dimers is demonstrated for photodimer D6. PhotoDSC was first used to thermally dissociate dimer D6 in a cyclic heat-isocool experiment at 160 °C in Figure 8(a), following the crystallization and melting behaviour of anthracene monomer A6 as it is formed. The crystallization enthalpy of A6, which only starts to show after some time (at the start of the experiment not enough monomer is present to crystallize and melt), increases with an increasing number of dissociation cycles. Subsequently, the photodimerization of the formed monomer A6 back into the dimer D6 is studied using a similar cyclic iso-heat-cool program with irradiation at 50 °C using 365 nm UVA light (5 W cm⁻², Figure 8(b)). The progress of the dimerization is again followed by the crystallization enthalpy, decreasing as the monomer is dimerized by the UVA light irradiation. The reversibility is clearly illustrated in the four additional thermal dissociation and photodimerization cycles shown in Figure 8(c).

Conclusions

Most anthracene derivatives and all photodimers found in literature are crystalline. The melting temperatures of the 9-substituted anthracene derivatives and dimers depend mostly on the length of the substituent chain, as these chains distort the crystal lattice, whereas the chemical structure of the substituent plays a minor role. Longer, aliphatic substituent chains result in lower melting temperatures for both dimers and monomers, as observed experimentally for substituent chains up to 14 atoms long. Conversely, the thermal dissociation behaviour of the studied photodimers was correlated to the electronic effects of the substituents, as expressed by their respective Hammett parameters \( \sigma_p \). The dissociation rates increase with increasing mesomeric electron-donating and electron-withdrawing substituent effects, with respect to the unsubstituted anthracene reference, implying the thermal stability decreases with stronger mesomeric substituent effects.

The maximum absorption wavelengths \( \lambda_{\text{max}} \) for the photodimerization of the anthracene derivatives shift to lower wavelengths for more negative Hammett parameters, however, this seems to go hand-in-hand with a decrease of the thermal stability. This might indicate that there is a practical limit to how far \( \lambda_{\text{max}} \) could be shifted towards the visible light spectrum for substitutions on the 9-position. Substituents with an even more negative \( \sigma_p \) parameter, e.g. by having a nitrogen atom next to the anthracene ring, may already thermally dissociate at ambient temperature.

The combined thermal and photochemical reversibility for the dimers, allowing bond formation in the near-visible light region and bond dissociation at more elevated temperatures, offers interesting opportunities for using functionalized anthracene dimer molecules as reversible crosslinks in polymer networks, as described in earlier work using dimer D5 in thiol-ene networks [31] and dimer D4 in polyurethane networks [32]. In contrast to thermoreversible reactions, such as the thermoreversible furan-maleimide Diels-Alder reaction, the thermal dissociation behaviour of these photodimers can be described as an ON/OFF kind of reactivity, where dissociation only occurs if a thermal stimulus is applied, while reassociation requires the photochemical stimulus. Combining the two, the conversion of the chemical reaction and the properties of the resulting polymeric materials can be tuned with precision.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors gratefully acknowledge the Fonds voor Wetenschappelijk Onderzoek (FWO) Flanders for the financial support for Project G006913N and the junior postdoctoral fellowship with grant number 12W4719N and Agentschap voor Innovatie door Wetenschap en Technologie (IWT, now VLAIO) for the PhD scholarship of Jonas Van Damme.
References

38. https://www.chemeo.com/cid/70 Anthracene%20photodimer