Chapter 3

Properties of reversible Diels-Alder furan/maleimide polymer networks as function of cross-linking density

Abstract
Thermally reversible thermosets based on furan functionalized polyketones cross-linked with (methylene-di-p-phenylene)bis-maleimide are synthesized. The number of furan groups present along the backbone and the cross-linker/furan molar ratio are varied. According to DSC measurements, the de-cross-linking temperature does not change significantly as function of the furan intake and its molar ratio with the cross-linker. All samples show an almost complete recovery of storage and loss modulus. The cross-linked samples are recycled up to seven times without significant quality loss in terms of mechanical properties. This suggests that a change in conformation does not result in different visco-elastic behavior. The most cross-linked sample is able to fully repair itself within 1 hour. A number of low cross-link density materials additionally show a shape memory effect.

3.1 Introduction
Thermosetting materials are often used because their properties differ from thermoplastic ones or because manufacturing technologies demand relatively low viscosity polymeric systems. Many of these materials are known to have, for example, a high modulus, high fracture strength, and good solvent resistance [1]. In addition, because cross-linked materials do not melt, they can be generally used in a broader temperature range than thermoplastic ones [2]. Thermosets are used in a number of applications, such as adhesives, coatings, rubbers, abrasives, polymer composites, electrical insulation, and printed circuit boards [3, 4].

Unfortunately, such excellent mechanical properties represent the main challenge once the need to reprocess, recycle, reshape or repair cross-linked materials occurs [5]. Re-workable thermosets aim at combining the positive properties of cross-linked materials with the processability and recyclability of thermoplastic ones [6]. The concept behind re-workable thermosets is that (part of) the polymer network can be de-cross-linked by applying an external stimulus, the latter being for example light [7] or heat. These networks can either consist of covalent or non-covalent cross-links. Examples of non-covalent reversible cross-links are based on hydrogen bonds [8, 9] and ionic [10] or Van der Waals interactions (e.g. SBS rubber) [11, 12]. All these physical bonds have been demonstrated to selectively break at a given de-cross-linking temperature. On the other hand, covalently reversible chemical cross-links are based on chemical bonds that can be broken by external influences, mainly heat or radiation energy. The most studied covalently thermo-reversible systems are based on the Diels-Alder (DA) reaction [13], probably because it ensures fast kinetics and a high number of recyclces with little, if any, degradation [14] between 50 °C and 200 °C.

In order to create a 3D cross-linked network, several systems have been employed based on the [4 + 2] DA reaction and its reverse. These systems consist of multiple dienophile and diene moieties of low molecular weight [15], dienes or dienophiles attached to polymer backbones cross-linked with bi-functional low molecular weight cross-linker, or polymeric chains containing both diene and dienophile [16].

Among the many chemical groups able to react via DA mechanism including fulvenes [17], cyclopentadiene [18, 19], anthracene [20] and others [21], the most investigated ones involves furan as diene and maleimide as dienophile [22]. The reason for this resides probably in the fast kinetics, which renders them attractive for potential industrial application.

In order to attach furan moieties to a polymer backbone, several methods have been studied mainly using polystyrene [23, 24] and polymethylacrylate [25-27] or epoxy resins [28] as polymeric precursors. However, the expensive synthetic routes and the use of solvents and catalysts render these modifications difficult to apply at industrial scale. A breakthrough into furan-based polymers has been previously accomplished in our research group [29]. Indeed, alternating polyketones synthesized by terpolymerization of carbon monoxide, ethene and propene were modified with furfurylamine through the Paal–Knorr reaction in order to obtain furanic pendent groups (Figure 3.1).
Figure 3.1 Paal-Knorr reaction of aliphatic alternating polyketones and furfurylamine (I) and subsequent cross-linking reaction with (methylene-di-p-phenylene)bismaleimide (II).

The synthesized polymer could be reversibly cross-linked with (methylene-di-p-phenylene)bismaleimide. The resulting material was recycled up to seven times without observing any significant deterioration of its mechanical properties. The reported system displayed several advantages as compared to similar ones presented in the literature [15-28]. In first instance, the use of the Paal–Knorr reaction to synthesize polymers with DA reactive groups showed several advantages typical of this modification, such as the absence of any catalysts or solvents, the presence of water as single by-product, fast kinetics and relatively high yields [29]. In addition, furfurylamine is a product based on furfural, a sugar based readily available chemical [30]. In our previous work, thermal and mechanical properties as measured by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and a 3-point bending test were used to study the reversibility efficiency of highly functionalized polyketone. The results obtained constitute in our opinion a breakthrough in the synthesis of recyclable thermosets since 100% healing and recyclability was found for several (up to seven) thermal cycles. Nevertheless, the reason for such a high recyclability, as compared to other systems described in literature, remained unknown and could possibly be related to the exceptionally
high diene (i.e furan) concentration, to the best of our knowledge never achieved before, anchored to the polymeric chains [15-28].

The present work aims at testing this hypothesis and obtaining a deeper insight into the mechanical and thermal behavior of the reported system as a function of the amount of DA reactive groups along the backbone. Indeed, polyketones with three different degrees of furan functionalization have been synthesized and cross-linking reactions at three different molar ratios of furan to maleimide were studied. Fourier transform infrared spectroscopy (FT-IR) and swelling studies were used to prove the reversibility while the healing efficiency and re-workability of the prepared materials were evaluated through DSC and DMTA studies.

3.2 Experimental

3.2.1 Materials

Alternating polyketones of ethylene, propylene and carbon monoxide were synthesized according to a reported procedure [31]. The olefinic part of the polyketone is constituted of 50 mol% ethylene and 50 mol% propylene (PK50, $M_w=5350$ Da). Furfurylamine (Sigma-Aldrich, >99%, The Netherlands), chloroform (Lab Scan, 99.5%, The Netherlands), and (methylene-di-p-phenylene)bismaleimide (Sigma-Aldrich, 95%, The Netherlands) were purchased and used as received.

3.2.2 Furan-derivatization of alternating polyketones

About 40 grams of alternating polyketone PK50 was weighed into a glass reactor fitted with a mechanical stirrer and a reflux condenser. The reactor was heated to a temperature of 110 °C and a specific amount of furfurylamine, depending on the desired carbonyl conversion, was added drop-wise for 1 hour. The reaction was allowed to proceed for another 3 hours. The reflux condenser was removed in the last hour to allow the produced water to evaporate. Three modified PK50 polymers were synthesized by using different amounts of furfurylamine (Table 3.1).

<table>
<thead>
<tr>
<th>Name</th>
<th>Polymer (g)</th>
<th>Furfurylamine (g)</th>
<th>Conv a (%)</th>
<th>$T_g$ b (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK50_20</td>
<td>40.95</td>
<td>6.31</td>
<td>20.1</td>
<td>26</td>
</tr>
<tr>
<td>PK50_40</td>
<td>46.81</td>
<td>14.4</td>
<td>39.9</td>
<td>44</td>
</tr>
<tr>
<td>PK50_60</td>
<td>44.71</td>
<td>20.75</td>
<td>57.7</td>
<td>55</td>
</tr>
</tbody>
</table>

Table 3.1 Quantities of alternating polyketone and furfurylamine used in Paal–Knorr synthesis of furan-modified polyketones (20, 40 and 60% of carbonyl groups) and their glass transition point. a) Carbonyl conversions based on the nitrogen content of the polymer, which was determined by elemental analysis. b) glass transition point ($T_g$) determined by DSC.
The dark brown products obtained were ground into small particles (by freezing the material if necessary). The particles obtained were washed with water, and then freeze-dried for 24 h. The carbonyl conversions were calculated on the basis of the nitrogen content of the final product according to the following formula:

\[
Conv = \frac{PK(g) \cdot [N \cdot 0.01]/(14 \cdot n) - PK(g) \cdot [N \cdot 0.01]/(14 \cdot n) + 2 \cdot PK(g) \cdot M_{\text{Water}} \cdot [N \cdot 0.01]/(14 \cdot n)]}{PK(g) \cdot M_{\text{PK}} - PK(g) \cdot M_{\text{Amine}} \cdot [N \cdot 0.01]/(14 \cdot n)}
\]

where \( M_{\text{PK}} \) represents the average molar mass of the repeating unit (calculated by considering the double carbonyl unit weighted in ethene and propene percentage), \( Conv \) represents the conversion of carbonyl groups, \( n \) is the number of nitrogen atoms in the repetitive unit of the reacted polyketone, \( N \) is the nitrogen percentage as determined by elemental analysis, \( M_{\text{Water}} \) and \( M_{\text{Amine}} \) are the molecular weight of water and the amine compound, respectively.

Below we report for each individual component the results of elemental analysis and, for all three, the most representative nuclear magnetic resonance spectroscopy (NMR) and FT-IR data.

\[
\text{PK50}_60: (\text{C}_6\text{H}_{12}\text{O}_2)_{40} (\text{C}_9\text{H}_{14}\text{N}_2)_{50} (112-140)_{40} (150-178)_{50}
\]
Calcd. C 71.8 H 6.6 N 5.1 O 16.4; Found C 73.7 H 7.3 N 5.1 O 13.9.

\[
\text{PK50}_40: (\text{C}_6\text{H}_{12}\text{O}_2)_{60} (\text{C}_9\text{H}_{14}\text{N}_2)_{40} (112-140)_{60} (150-178)_{40}
\]
Calcd. C 71.1 H 5.6 N 3.4 O 19.8; Found C 71.1 H 7.3 N 3.7 O 17.9.

\[
\text{PK50}_20: (\text{C}_6\text{H}_{12}\text{O}_2)_{80} (\text{C}_9\text{H}_{14}\text{N}_2)_{20} (112-140)_{80} (150-178)_{20}
\]
Calcd. C 70.4 H 4.6 N 1.7 O 23.2; Found C 68.8 H 7.6 N 2.0 O 21.6.

IR (KBr): 3112 (m, CH), 1700 (vs, C=O), 1436 (m, ring stretching), 1345 (m, ring stretching), 1073 (m, C=C stretching), 1013 (m, C=C stretching), 734 (m, C=H out-of-plane bending).

\(^1\)H-NMR (CDCl\textsubscript{3}): \( \delta = 7.3 \) (d, furan), 6.2 (br, furan), 5.9 (br, furan), 5.8 (br, pyrrole), 4.9 (br, pyrrole).

3.2.3 Cross-linking of furan modified polyketones

About 15 grams of modified polyketone and a stoichiometric (with respect to the furan groups) amount of (methylene-di-p-phenylene)-bis-maleimide were dissolved in 150 g of CHCl\textsubscript{3} in a round bottom flask fixed with a magnetic stirrer (see Table 3.2 for an overview of all prepared samples). The reaction mixture was heated to 50 °C, and the reaction was allowed to proceed until gelation took place.

The cross-linked polymers were isolated after removing the gel from the bulb and drying them to constant weight at 50 °C under vacuum. The samples have been coded by stating the ethene content of polyketone, the carbonyl conversion level and the maleimide / furan ratio (i.e., PK50\textsubscript{60-M1}). Below we report the most relevant FT-IR peaks for the cross-linked polymers.
Table 3.2 Cross-linking reactions between furan modified polyketones and bismaleimide.

<table>
<thead>
<tr>
<th>No.</th>
<th>Conv(^a) (%)</th>
<th>Maleimide:Furan Ratio</th>
<th>Polymer (g)</th>
<th>Bismaleimide (g)</th>
<th>(T_g)(^b) (°C)</th>
<th>(T_{\text{rDA}})(^c) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK50_60_M1</td>
<td>60</td>
<td>1:1</td>
<td>15.01</td>
<td>9.10</td>
<td>102</td>
<td>136</td>
</tr>
<tr>
<td>PK50_60_M2</td>
<td>60</td>
<td>1:2</td>
<td>15.01</td>
<td>5.00</td>
<td>86</td>
<td>141</td>
</tr>
<tr>
<td>PK50_60_M4</td>
<td>60</td>
<td>1:4</td>
<td>14.97</td>
<td>2.45</td>
<td>64</td>
<td>127</td>
</tr>
<tr>
<td>PK50_40_M1</td>
<td>40</td>
<td>1:1</td>
<td>15.25</td>
<td>7.23</td>
<td>88</td>
<td>124</td>
</tr>
<tr>
<td>PK50_40_M2</td>
<td>40</td>
<td>1:2</td>
<td>15.06</td>
<td>3.57</td>
<td>51</td>
<td>130</td>
</tr>
<tr>
<td>PK50_40_M4</td>
<td>40</td>
<td>1:4</td>
<td>15.19</td>
<td>1.79</td>
<td>34</td>
<td>155</td>
</tr>
<tr>
<td>PK50_20_M1</td>
<td>20</td>
<td>1:1</td>
<td>14.75</td>
<td>3.84</td>
<td>58</td>
<td>123</td>
</tr>
<tr>
<td>PK50_20_M2</td>
<td>20</td>
<td>1:2</td>
<td>15.03</td>
<td>1.97</td>
<td>30</td>
<td>125</td>
</tr>
<tr>
<td>PK50_20_M4</td>
<td>20</td>
<td>1:4</td>
<td>15.10</td>
<td>0.97</td>
<td>20(^c)</td>
<td>n.d.(^d)</td>
</tr>
</tbody>
</table>

\(^a\) 1-4-di-carbonyl conversion as defined in the experimental part; \(^b\) Calculated as peak of tan(\(\delta\)) in DMTA analysis; \(^c\) Calculated as peak of the rDA exotherm in DSC analysis; \(^d\) no \(T_{\text{rDA}}\) detected.

3.2.4 Characterization

\(^1\)H-NMR spectra were recorded on a Varian Mercury Plus 400 MHz NMR apparatus using CDCl\(_3\) or DMSO-d6 as solvents. IR spectra were recorded using a Perkin Elmer Spectrum 2000 FT-IR apparatus. DSC spectra were recorded on a Perkin Elmer DSC Pyris 1 from 20 °C to 180 °C at a rate of 10 °C per minute. DMTA measurements were performed on a Rheometrics scientific solid analyzer (RSA II) under air environment using dual cantilever mode at an oscillation frequency of 1 Hz at a heating rate of 3 °C per minute. DMTA specimens were 6 mm wide, 1.4 mm thick and 54 mm long. DMTA samples were obtained by weighing 0.5 g of the polymer into a mold and pressing them for 20 minutes at a temperature of 120 °C and a pressure of 4 MPa [29]. Subsequently, the samples were cross-linked in the mold for 24 hours at 50 °C and 4 MPa. Each sample was tested for six cycles between room and softening temperature and then treated at 50 °C for 24 hours, after which the final (7\(^{th}\)) measurement was performed. An isothermal DMTA measurement was performed at 50 °C. The sample was prepared identically to those for the temperature sweep measurements, except for a de-cross-linking step after the measurement by heating the sample at 120 °C for 1 hour. The sample was then quenched in an ice bath after which a second DMTA measurement was performed immediately.

Cross-link density was measured by swelling experiments in chloroform: 700 mg of dried cross-linked polymers were weighed into 20 ml vials and 10 mL of chloroform was added. The polymer was allowed to swell for 14 days after which the chloroform was removed over a glass filter and the weight of the swollen
polymer was measured. Each sample was measured in duplo, with the second sample being submersed for 1 more day, to ensure that the swelling had reached equilibrium.

The cross-link density ($C_{\text{Cross-link}}$) was calculated using the Flory-Rehner equation (Equation 2), where $V_p$ is the volume fraction of the polymer in the swollen gel, $V_s$ is the molar volume of the solvent, and $\chi$ is the interaction parameter of chloroform with the modified polyketone. The latter was calculated from the solubility parameters of the cross-linked polyketone ($\delta_p$) and chloroform ($\delta_s$) according to equation 3 [32].

$$C_{\text{Cross-link}} = \frac{\ln(1-V_p) + V_p + \chi \cdot V_p^2}{V_s (0.5 \cdot V_p^{1/3})}$$  \hspace{1cm} 2

$$\chi = \frac{V}{RT} (\delta_s - \delta_p)$$  \hspace{1cm} 3

The parameter $\chi$ resulted to be particularly small because of the similarity between the solubility parameter of the cross-linked network and chloroform. The corresponding term in Equation 2 could then be neglected in the calculation of the cross-linking degree.

3.3 Results and discussion

3.3.1 Synthesis of polyketone adduct with furanic pendent groups

The furan functionalization of polyketones was performed by the reaction of PK50 with furfurylamine in bulk at a temperature of 110 °C. The reaction proceeded to full conversion of furfurylamine in 4 hours. Carbonyl conversions of 20, 40, and 60% were targeted and obtained as result of the reaction (Table 3.1). The obtained polymers are dark brown and show increasing softening temperatures with increasing concentrations of furfurylamine. The lowest concentration of furfurylamine (20%) yields a product with waxy appearance and high viscosity at room temperature. The other samples appeared as brownish solids.

DSC measurements of the obtained modified polyketones (Table 3.1) showed that a higher degree of modification resulted in an increased $T_g$. This is obviously related to the increase in the concentration of aromatic (pyrrolic) groups along the polymer backbone.

The furfurylamine conversion was found to be 100% for all samples, in agreement with the reactivity described in our previous work [29]. $^1$H-NMR measurements (Figure 3.2 left) showed the formation of broad peaks at 5.8 and 4.9 ppm, which are assigned to the pyrrole ring in the backbone and the $\text{CH}_2$ attached to the pyrrole and furan ring, respectively. Moreover, broad peaks at 7.3, 6.2 and 5.9 were observed and assigned to the hydrogen atoms of the furan rings connected to the polymer backbone. Moreover, all these relevant peaks are shown (Figure 3.2) to increase in intensity, as expected, with the furan concentration. This is in agreement with our previous results on this system [29].

FT-IR spectroscopy (Figure 3.2 right) showed that the peak at 1464 cm$^{-1}$ ($\text{CH}_2$ scissoring) [33] becomes smaller with decreasing 1,4-dicarbonyl content as well as the peaks at 1361 cm$^{-1}$ ($\text{CH}_2$ wagging) and 1395
cm$^{-1}$ (CH$_2$ twisting) while new peaks appeared at 1436 cm$^{-1}$ and 1345 cm$^{-1}$ (pyrrole and furan ring stretching) [34]. Furthermore, a split of a band at 1050 cm$^{-1}$ (ν C–C aliphatic stretching) [33] present in PK50 lead to the appearance of two new peaks at 1013 cm$^{-1}$ and 1073 cm$^{-1}$ (pyrrole and furan C=C stretching) [35], whose intensity increase with furan and pyrrole concentration. A shift of the peak at 772 for cm$^{-1}$ (rocking CH$_2$) [33] towards lower wavelength (i.e., 734 cm$^{-1}$, ν C–H out-of-plane aromatic rings) confirmed the increased percentage of aromatic groups along the backbone.

**Figure 3.2** $^1$H-NMR (left) and FT-IR (right) spectra of unmodified polyketone (PK50, (a)) and furan modified polyketones (20, 40 and 60% conversion of carbonyl groups). (PK50_20 (b), PK50_40 (c) and PK50_60 (d)). Spectra are normalized with respect to the peak at 2967 cm$^{-1}$ (ν CH$_3$).

### 3.3.2 Cross-linking of furan functionalized polyketones and network swelling properties

Cross-linking via the DA reaction is indicated by FT-IR (Figure 3.3), which shows that the C-O-C ether peak of reacted furan (1182 cm$^{-1}$) [29] becomes stronger at higher concentrations of bis-maleimide (insert Figure 3.3).

**Figure 3.3** IR spectra of PK50_20 cross-linked with 1:1 (PK50_20_M1) (a), 1:2 (PK50_20_M2) (b) and 1:4 (PK50_20_M4) (c) maleimide/furan ratios.
The peak at 1013 cm\(^{-1}\) and (pyrrole C-H in plane bending), 1073 cm\(^{-1}\) (pyrrole and furan C-C stretching) decreased with higher concentrations of bis-maleimide. A new peak appeared at 1378 cm\(^{-1}\) (C-N stretching in maleimide rings), which confirmed the presence of bis-maleimide.

The network formation has been studied from a kinetic (gelation time) as well as equilibrium (swelling and cross-linking density) point of view. The gelation time during cross-linking of furan modified polyketones with (methylene-di-p-phenylene)bis-maleimide was studied as a function of the amount of furan functionalization (20, 40 and 60% carbonyl conversion) and the molar ratio between the maleimide and furan moieties (1:1, 1:2 or 1:4) (Table 3.3).

<table>
<thead>
<tr>
<th>No.</th>
<th>Gelation time (h)</th>
<th>Swelling (%)</th>
<th>Cross-link density (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK50_60_M1</td>
<td>3</td>
<td>174</td>
<td>1.50</td>
</tr>
<tr>
<td>PK50_60_M2</td>
<td>4-5</td>
<td>261</td>
<td>0.86</td>
</tr>
<tr>
<td>PK50_60_M4</td>
<td>5-5.5</td>
<td>402</td>
<td>0.39</td>
</tr>
<tr>
<td>PK50_40_M1</td>
<td>3.5</td>
<td>202</td>
<td>1.24</td>
</tr>
<tr>
<td>PK50_40_M2</td>
<td>15.5</td>
<td>306</td>
<td>0.64</td>
</tr>
<tr>
<td>PK50_40_M4</td>
<td>17</td>
<td>423</td>
<td>0.35</td>
</tr>
<tr>
<td>PK50_20_M1</td>
<td>24</td>
<td>228</td>
<td>0.87</td>
</tr>
<tr>
<td>PK50_20_M2</td>
<td>72</td>
<td>464</td>
<td>0.31</td>
</tr>
<tr>
<td>PK50_20_M4</td>
<td>144</td>
<td>725</td>
<td>0.14</td>
</tr>
</tbody>
</table>

**Table 3.3** Calculated cross-link densities of cross-linked functionalized polyketones. The gelation time has been calculated according to a procedure described in a previous paper [29].

The gelation time is at its minimum, for every given furan content, at equimolar maleimide/furan ratios. It increases for samples with excess furan because of the shortage in cross-linker (bis-maleimide) concentration. This result is in agreement with the results reported by Zhang et al. [29], who performed a similar experiment with 80% carbonyl conversion and different maleimide:furan ratios. The gelation time also increases for the modified polyketone with less pending furan groups (Table 3.3). This is probably related to the average amount (per chain) of furan groups and ultimately to the kinetics of the DA reaction.

The above considerations point in the direction of an inverse correlation between gelation time and cross-link density, as normally observed also for other polymeric networks [36]. This hypothesis is confirmed by the cross-link density values (Table 3.3) determined from swelling experiments (see experimental part).

Furthermore, the equilibrium swelling values (Table 3.3) are found to be inversely proportional to the cross-link density. This is in agreement with other studies reported in the literature for similar systems. Indeed, Chujo et al. [37] reported the same observations by analyzing a thermo-reversible hydrogel prepared by using two poly(oxazoline)s: one with pending maleimide groups and one with pending furan ones. The
authors showed that the swelling of the cross-linked polymers decreased with increasing amounts of cross-links. Cross-linking of furan-modified epoxy-resins with an aromatic bis-maleimide was tested by Peterson et al. [38] who stated that changes in cross-link density are primarily responsible for equilibrium swelling. In this respect, the PK systems studied in this work seems to behave in agreement with other similar systems.

3.3.3 Thermal properties of cross-linked polyketones

Multiple cycles of the Diels-Alder (DA) and retro Diels-Alder (rDA) reaction were investigated by DSC. The initial cycle of each measurement was ignored because of possible influences from the evaporation of residual solvent and chain reorientation effects. Similar to the results described in our previous work, all samples showed mainly one broad endothermic transition in the 120–140 °C range, thus suggesting the presence of only one of the two possible adducts [39]. The integral of the DSC peaks represents the total amount of heat adsorbed during the rupture of the DA bonds [28]. The latter values (Figure 3.4) for consecutive thermal cycles at different maleimide/furan ratios can be interpreted as kind of a “thermo-recovering degree” [40]. It is worth noticing how at a fixed furan content, the integral decreases towards lower cross-linker concentrations (i.e., when going form maleimide/furan ratio of 1:1 up to 1:4).

This can be easily explained if one takes into account that, at lower bis-maleimide concentrations, less cross-linking points are formed. The differences in the endotherms as function of the thermal cycles indicate a high level of DA recovery and in any case much higher than for similar systems reported in the literature [14, 21, 38, 39, 41].

Figure 3.4 Integrals for rDA endothermic peak in consecutive thermal cycles (1, 2 and 3) for PK50_20, PK50_40 and PK50_60 cross-linked at 1:1 (M1), 1:2 (M2), and 1:4 (M4) maleimide/furan ratios.
However, it must be noted that in all measurements (thus independently of the furan content and its molar ratio with the maleimide) the integral values decrease, although slightly, with each cycle performed. A possible explanation for this effect is that the material does not have enough time to completely recover as the DA adduct [29], which means that less energy will be absorbed during the next cycle.

In order to check this hypothesis, extra DSC experiments were performed, where the samples were kept isothermally at 50 °C for 30 minutes between each cycle (2 and 3 in Table 3.4). The same samples were then stored at 50 °C for 24 h, after which another three cycles (with again 30 min. annealing for 5 and 6 in Table 3.4) were performed to study how the material recovers during longer treatment at 50 °C.

<table>
<thead>
<tr>
<th>No.</th>
<th>Cycle 1 (J/g)</th>
<th>Cycle 2 (J/g)</th>
<th>Cycle 3 (J/g)</th>
<th>Cycle 4 (J/g)</th>
<th>Cycle 5 (J/g)</th>
<th>Cycle 6 (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK50_60_M1</td>
<td>27.7</td>
<td>22.9 (-17.6%)</td>
<td>19.5 (-14.8%)</td>
<td>19.2 (-1.5%)</td>
<td>17.5 (-9.1%)</td>
<td>16.2 (-7.2%)</td>
</tr>
<tr>
<td>PK50_40_M1</td>
<td>23.7</td>
<td>22.6 (-4.6%)</td>
<td>20.8 (-7.9%)</td>
<td>19.4 (-6.7%)</td>
<td>17.5 (-9.8%)</td>
<td>17.7 (+0.9%)</td>
</tr>
<tr>
<td>PK50_20_M1</td>
<td>20.0</td>
<td>17.9 (-10.2%)</td>
<td>16.4 (-8.2%)</td>
<td>18.0 (-9.8%)</td>
<td>16.6 (-8.0%)</td>
<td>15.6 (-6.2%)</td>
</tr>
</tbody>
</table>

Table 3.4 Calculated integrals for rDA endothermic peak in consecutive DSC cycles after 30 minutes isothermal DSC at 50 °C (cycles 1, 2 and 3) and after treatment of samples at 50 °C for 24 h (cycles 4, 5 and 6) of PK50_20, PK50_40 and PK50_60 at 1:1 maleimide/furan ratio (M1).

The results show that with an annealing step of either 30 minutes or 24 h for DA re-cross-linking, there is still a loss in area under the curve. In fact, the average loss in area is similar to the DSC samples that were not kept isothermally at 50 °C; in both cases the average loss over the first three cycles being similar. This could suggest that either the annealing step was too short to reform all cross-links or, for every sample and every thermal cycle, a different equilibrium value of the cross-linking density is attained in time. Yet another possibility would be related to the difference in enthalpy values between the two possible DA adducts (see above). The latter hypothesis (i.e., a change in the relative concentration of the endo and exo adducts during the thermal cycles) is partially suggested also by the form of the DSC thermograms. Indeed, the rDA endotherm peaks shifted to higher temperature in the second three cycles with respect to the former ones, indicating the formation of the most thermodynamically stable adduct [39]. Interestingly, Tian et al. [28] noted the same behavior in the presence of a di-epoxy furan adducts and the same aromatic bis-maleimide used in this study. However, the authors attributed this behavior to increased cross-linking density of the epoxy part that somewhat hinders recovery of the DA bonds.

Such dynamic exchange between the two possible adducts as function of the thermal history constitutes in our opinion a very important result since it allows tailoring the rDA temperature as function of the thermal history.
When studying the cross-linking behavior as function of the maleimide/furan ratio, three observations can be made. Indeed, at relatively low maleimide/furan ratio the r-D.A transitions become broader (Figure 3.5) and shifted asymmetrically towards lower temperatures, while the cross-linking density drops significantly.

This could be related to the presence, as the furan content decreases, of longer PK chains (with a $T_g$ of about $-15^\circ$C), thus increasing the overall mobility of the chains [42].

DMTA was used to study the storage and loss modulus of the cross-linked materials between 30 and 110 $^\circ$C. The production of the test-specimen is already proof for thermally reversible cross-linking, since the polymer samples were pressed in a hot mold using samples that were cross-linked in solution. This would have been impossible with non-reversible cross-links.

Due to low mechanical strength, no DMTA results were obtained for product PK50_20_M4. The results (Figure 3.6) showed that the moduli of all products declined rapidly above a given temperature. This transition temperature, above which the material shifts from an elastic phase to a viscous one, is obtained by evaluating the corresponding tan ($\delta$) peaks.
Figure 3.6 Loss (Δ) and storage (□) modulus behavior in DMTA cycles from 30 °C till 110 °C for PK50_60 (Figure on the left), PK50_40 (Figure in the center) and PK50_20 (Figure on the right) at 1:1 (M1) (a), 1:2 (M2) (b) and 1:4 (M4) (c) maleimide/furan ratios and tan (δ) of the respective samples (Figures at the bottom).

The broadening of the latter as well as the remarkable shift of the maximum towards lower peak-temperatures at relatively low furan content are probably related to the decreased concentration of aromatic groups (both pyrrolic and furan ones) along the polymer backbone.

For all prepared systems, the thermal reversibility proved to be in line with the one shown in our previous work [29]. Indeed, very similar values of both moduli (storage and loss ones) are observed in 7 consecutive cycles. This can be easily checked by plotting the tan (δ) values as function of the cycle number for three samples (Figure 3.7 for samples PK50_60_M1, PK50_60_M2 and PK50_40_M1) at a temperature of 50 °C (i.e. the temperature at which the cross-linking takes place).
Figure 3.7 Loss tangent retention at 50 °C after DMTA cycles from 30 till 110 °C for PK50_60_M1 (a), PK50_60_M2 (b) and PK50_40_M1 (c).

In the 7th cycle, a regeneration of the DMTA bar has been attempted by keeping it in the oven for 24 h at 50 °C. In all of these samples, the tan (δ) is lower in the first and last cycle of the measurement. This is in complete agreement with results already found in our group [29] and demonstrates the outstanding robustness of furan modified polyketones in terms of the thermal recovery efficiency independently of the furan content. The high efficiency in the thermal recovery of the mechanical properties is in contrast with the loss in the DSC integrals (see above). In order to get further insight, a DMTA measurement was performed on a de-cross-linked sample at 50 °C. A DMTA sample of compound PK50_60_M1 was de-cross-linked at 120 °C for 1 h, after which the sample was quickly cooled. Subsequently, an isothermal DMTA measurement at 50 °C was performed, showing a monotonous increase in the storage modulus and a decrease in the loss one for 1 h. This suggests that cross-linking is taking place at 50 °C and is complete (in terms of mechanical behavior) after 1 h. According to this, an annealing at the same temperature for 24 h (Table 3.4) should be sufficient to ensure recombination of all DA bonds during the DSC measurements. This is however not the case since even after the annealing step a loss in the DSC integrals was observed.

These considerations clearly suggest that complete reversibility at molecular level (both in terms of amount and kind of DA adduct formed) is not a necessary condition for the achievement of reversibility at the macromolecular one (i.e. in terms of mechanical behavior). This constitutes, to the best of our knowledge, an important principle for the design of new re-workable polymers.

The thermal and mechanical behavior of these newly prepared materials clearly demonstrate the flexibility of modified aliphatic polyketones in providing, through the DA chemistry, new materials with tunable mechanical properties as function of their chemical structure. This is further confirmed by an unpredicted result of this project.

Indeed, at the end of the DMTA measurements, all bars have been air quenched and remained in a deformed state in almost all cases. However, samples from compounds PK50_40_M2, PK50_40_M4, and PK50_20_M2 recovered their initial shape after treatment at 50 °C for 24 h (Figure 3.8).
Figure 3.8 PK50_40_M1 sample shape-memory. The sample before DMTA measurements (a) has been deformed by the test (b) and returned to its original shape after being stored at 50 °C (c).

This property is known as a shape memory, and is most likely the result of the cross-links that are still intact after DMTA test. Upon treatment at 50 °C, the polymers are above their T_g and as a result there is enough flexibility in these materials to return to their initial shape. Because the cross-links in these materials are only reversible above 120–140 °C, the memorized shape obtained during molding can be reset at 50 °C.
3.4 Conclusions

The results presented in this chapter show the successful synthesis and cross-linking of polyketones with varying amounts of furan groups. Cross-link density measurements show that higher furan intakes and maleimide concentrations both lead to higher cross-link densities as well as shorter gelation times. DSC measurements show that the de-cross-linking temperature is only marginally influenced by the furan and maleimide concentrations. However, the rDA enthalpies steadily decrease, although only slightly, for different thermal cycles.

Isothermal DMTA measurements reported that the most cross-linked samples regain their original strength in 1 h after treatment at 50 °C. The $T_g$ of these materials can be finely tuned by using the right amount of furfurylamine (during the PK modification step) and cross-linker.

In general, it must be stressed how all obtained materials are reworkable at 120–150 °C, and can be recycled up to seven times without significant loss in DMTA performance. A very interesting and, to the best of our knowledge, unique result is booked here. Indeed, from an applicative point of view, this demonstrates the robustness of the furan-modified PK system, showing almost full mechanical reversibility (e.g. loss and storage modulus during thermal cycling), independently of the furan intake. At the same time, polyketones show an extreme versatility since control over the furan modification reaction allows preparing different thermo-reversible materials with an expanded range of available thermal (e.g., $T_g$) and mechanical properties. From a more scientific point of view, the results obtained suggest that complete reversibility at molecular level (as estimated by DSC studies) is not a necessary condition for obtaining a complete reversible mechanical behavior (as shown by DMTA data).
3.5 References

[34] Spoto, G.; Geobaldo, F.; Bordiga, S.; Lamberti, C.; Scarano, D.; Zecchina, A. Top. in Cat. 1999, 8, 279.