Functional polymers from alternating aliphatic polyketones

Toncelli, Claudio

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Chapter 4

Cyclopentadiene-functionalized polyketone as self-cross-linking reversible thermoset

Abstract
Self-cross-linkable thermo-reversible thermosets were obtained by a two-steps post-functionalization of aliphatic alternating polyketones. During the first step, chlorine-pendant groups connected to pyrrolic units along the polyketone backbone were introduced by the Paal-Knorr chemical modification. Two materials, containing different cyclopentadiene functionalization levels of 9 and 22 % (with the respect of initial 1,4-dicarbonyl units), were produced. Thermo-reversibility was proven by gelation experiments and the thermo-mechanical properties of the obtained thermosets were evaluated by DSC and DMTA analysis. DSC integrals displayed a broad transition varying from 75-100 °C till 160 °C, which can be related to retro-Diels Alder de-cross-linking of the dicyclopentadienyl moieties. The DMTA analysis showed the complete thermo-mechanical recovery of the material up to six thermal cycles with a softening temperature around 210 °C. Such outstanding thermal stability of the resulting thermosets can be preliminarily explained with the probable formation (suggested also by the DSC analysis) of cyclopentadienyl trimers. Independently of the exact mechanism at the molecular level, it must be noticed that all prepared materials retained their mechanical behavior during at least 6 consecutive thermal cycles, thus indicating the re-workability of the system.
4.1 Introduction

Thermosetting polymers differ from thermoplastics by the formation of a 3-dimensional network of covalent intermolecular bonds. The latter creates a rigid network [1], therefore they show relatively high creep resistance, high modulus, dimensional stability at high temperatures and chemical resistance [2]. These properties are well-suited for applications such as adhesives, coatings, rubbers, polymer composites, electrical insulation, and printed circuit boards [3, 4].

On the other hand, this network is difficult to re-process without initiating its degradation, which ultimately leads to irreversible deterioration of the mechanical behavior [5]. One possible approach towards fully recyclable thermosts is the use of reversible cross-linking points that undergo de-cross-linking without affecting the backbone structure [6]. An external stimulus, such as pH, light [7] or heat may be applied for the selective scission of the cross-linking bridges. The reversible cross-linking interaction might be non-covalent, e.g. hydrogen bonds [8, 9] and ionic [10] or Van der Waals interactions (e.g. SBS rubber) [11, 12]. However, covalently reversible chemical cross-links represent a more popular choice, due to their higher bond energy and thermal stability.

Among the available thermo-reversible systems, the [4+2] Diels-Alder (DA) cycloaddition is the most investigated one [13] since it ensures fast re-convertibility and recyclability without any significant loss in mechanical properties during repetitive processing steps [14].

Furan and maleimide groups as diene and dienophile, respectively, represent the simplest choice in terms of application temperature window (50-160 °C) [15-17].

When bi-functional diene and dienophile are employed, this produces a linear polymer, while 3D thermoset networks can be obtained by using poly-functional monomers or pre-polymers. For the latter case, several polymer matrixes were employed for post-modification purposes, such as polystyrene [18, 19] and polymethylacrylate [20-22] or epoxy resins [23]. However, the expensive and troublesome routes for the synthesis of furan or maleimide-functionalized macro-monomers and polymers prohibit the up-scaling of the concept to commercial applications. Post-modification of polyketones was presented as a potential low cost alternative in a previous publication of our group [24]. Alternating aliphatic polyketones, synthesized by terpolymerization of carbon monoxide, ethene and propene, were modified through the Paal-Knorr reaction with furfurylamine to introduce furanic groups along the backbone. In combination with (methylene-di-p-phenylene)bismaleimide, the obtained thermo-set could be recycled up to 7 times without observing any significant loss of mechanical properties. The employed functionalization reaction (i.e. Paal-Knorr) is particularly attractive since neither a catalyst nor solvents are employed; the reaction displays fast kinetics relatively high yields and water is formed as single by-product [24]. The softening temperature (as determined by DMTA) of the corresponding reversible network as well as, to some extent, the de-cross-linking one (as determined by DSC) can be tuned by varying the degree of furan functionalization, while the cross-linking degree can be tuned by varying the furan to maleimide molar ratio [25].
Despite the advantages outlined above, furan-maleimide Diels-alder chemistry is not suitable for applications above 150 °C. In this respect, first Kennedy and Castner [26] and subsequently Chen and Ruckenstein [27], showed that the cyclopentadiene-based DA/rDA chemistry provides a thermo-reversible system displaying a higher thermo-reversibility temperature. In the first case, the authors carried out a reaction between dicarboxylate dicyclopentadienyl DA adducts and polyolefins, such as isopropylene isobutylene rubbers (IIR) and ethylene propylene rubbers (EPM), to create an ester bridge between the polymer backbone and the DA adduct. Such cyclopentadiene-modified polymers showed de-cross-linking at 215 °C and re-processability of the thermosets at temperatures above 170 °C, thus suggesting that, even though at this temperature the DA bonds are only partially broken, the macromolecular chains are free to stretch and slide upon shear.

In 2008, Murphy et al [28] revised an old system invented by J.K.Still and L.Plummer [29] to synthesize a dicyclopentadiene connected cyclically by aliphatic ester bridges. This system showed, during DSC measurements, an exotherm at 129.4 °C that can be attributed to DA polymerization and a large rDA endotherm peak at higher temperatures (e.g. 130-180 °C, DSC measurements performed till 180 °C) while DMTA measurements showed a softening temperature of 138 °C. Moreover, the DA dicyclopentadienyl adduct contains two distinct C=C bonds that could act as dienophile in further cross-linking reaction: the norbornene bond and the cyclopentene bond. While it is the more reactive norbornene double bond that acts as dienophile for the formation of the unsubstituted cyclopentadiene trimer, Murphy et al. [28] found that it is the less hindered cyclopentene double bond that acts as dienophile in the formation of the carboxy-substituted trimers. This indicates, in first instance, the possibility for cyclopentadienyl groups to react via a “polymerization” mechanism according to which the formation of trimers and higher oligomers can take place. Furthermore, this suggests also that the temperature at which rDA is occurring might be significantly influenced by the kind of aggregates (i.e. dimers or higher oligomers) formed during cross-linking.

In this paper, we describe the synthesis cyclopentadiene functionalized polyketone synthesized via the route illustrated in Figure 4.1.

Figure 4.1 Synthesis of cyclopentadiene-modified polyketones
The synthesis of the chloride functional polymer \((\text{PKCl, III})\) is carried out by reaction of amino-propyl chloride with an aliphatic polyketone (50/50 molar ratio propene/ethene). The polymer structure is studied by \(^1\text{H}-\text{NMR}\) and FT-IR measurements. Subsequently, the reaction of this intermediate with lithium cyclopentadienyl (IV) results in polymers with different functionalization degrees (V). Their structures are confirmed by FT-IR studies and elemental analysis calculation. Furthermore, the thermal reversibility is tested and analyzed by DSC measurements and gelation experiments while the thermo-mechanical properties of the obtained thermosets are determined by DMTA analysis.

4.2 Experimental

4.2.1 Materials
The alternating polyketones, co- and terpolymers of carbon monoxide, ethene, and propene, with 50% ethylene (PK50, MW 5350 Da) on the basis of the total olefin content were synthesized according to a reported procedure [30]. Tetrahydrofuran (Acros, >99%) and dichloromethane (Lab-Scan, 99.8%) were purchased and distilled from CaH\(_2\) (Sigma-Aldrich, 99%) before use. 3-Chloropropylamine (Sigma-Aldrich, >99%) and lithium cyclopentadiene (Sigma-Aldrich, >99%) were purchased and used as received.

4.2.2 Frontier molecular orbital (FMO) calculations
FMO calculations were performed with HyperChem Release 8.0. The molecular orbital energy levels were calculated based on a simulation that uses an \textit{ab initio} calculation method. For this reason the small 3-21G basis set was used. All the relevant molecules were simulated and the resulting energy levels were compared to yield the HOMO-LUMO energy gaps.

4.2.3 Characterization
\(^1\text{H}-\text{NMR}\) spectra were recorded on a Varian Mercury Plus 400 MHz apparatus. CDCl\(_3\) was used as the solvent. FT-IR spectra were recorded using a Perkin-Elmer Spectrum 2000 equipped with a heating stage and temperature controller. DSC analysis was performed using a Perking-Elmer differential scanning calorimeter Pyris 1 under N\(_2\) atmosphere from 20 °C to 180 °C at a rate of 10 °C per minute. Elemental analysis was performed using a Euro EA elemental analyzer. DMTA measurements were performed on a Rheometrics scientific solid analyzer (RSA II) under air environment using dual cantilever mode at an oscillation frequency of 1Hz at a heating rate of 3 °C per minute. Samples were 5.8 mm wide, 1.3 mm thick and 54 mm long. These sample bars were pressed for 20 minutes at 190 °C and 4 MPa. Afterwards, the samples were cross-linked in the mold for 24 hours at 50 °C and 4 MPa. Each sample was tested for 6 consecutive cycles between room and softening temperature.
4.2.4 Chlorine-derivatization of alternating polyketones

About 40 grams (253 mmol of 1,4-dicarbonyl repeating units) of alternating polyketone PK50 was weighed into a glass reactor fitted with a mechanical stirrer and a reflux condenser. In the meantime, 26.3 g (0.8 eq with the respect to 1,4-dicarbonyl groups) of 3-chloropropylamine hydrochloride were solubilized in 200 ml methanol and neutralized with 1 eq. of NaOH. Afterwards, the amine solution was added drop-wise for 1 hr to the reactor mixture, previously heated up to 110 °C. During the last half-hour of the reaction, the reflux condenser was taken off in order to let the remaining solvent evaporate. After four hours of reaction, the crude mixture was grinded and then washed with 2 L of demi-water for several times to remove any unreacted amine (the filtrate has been analyzed by GC/MS in order to check when the product was well purified). The product was then filtered and freeze-dried for 24 hrs. The reaction yielded a light brown product (PKCl).

The carbonyl conversion was calculated on the basis of the nitrogen content of the final product (N) according to the following formula:

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

where \(M_{\text{PK}}\) represents the average molecular mass of the 1,4-dicarbonyl repeating unit, \(Conv\) 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 calculated by elemental analysis, \(M_{\text{Water}}\) and \(M_{\text{Amine}}\) are the molecular weight of water and the amine compound, respectively. PKCl showed a carbonyl conversion of 55.0 %. The most relevant data from the characterization are reported below.

Elemental analysis (EA): Calcd. C 65.45; H 7.81; Cl 11.64; N 4.60; O 10.50. Found C 63.91; H 7.86; Cl + O 23.69; N 4.53.

\(^1\)H-NMR (CDCl3): 1.04 (CH3-CH aliph.); 1.83 (CH3-CH arom.); 1.94 (Cl-CH2-CH2); 2.2-3.1 (CH2 aliph.); 3.50 (CH2-Cl); 3.87 (N-CH2); 5.45-5.95 (CH arom.)

FT-IR (cm\(^{-1}\)): 667 (C-Cl bending); 749 (C-Cl stretching); 1039 (C-H in plane deformation); 1399 (C-N ring stretching) 1457 (C=C stretching); 1704 (C=O carbonyl stretching); 2875-2935 (stretching C-H aliphatic); 2969 (stretching C-H pyrrole).

4.2.5 Cyclopentadiene-functionalized polymer (PKCPD1 and PKCPD2)

PKCl was then used as reactant in the second synthetic step with Li-cyclopentadiene. The latter was added in 0.5 equivalents (PKCPD1) and equimolar amount (PKCPD2) to the concentration of chloride groups calculated according to the elemental analysis. The reaction was carried out under N2 using THF as the
solvent. The reaction was then set at 30 °C for 18 hours. Afterwards, the mixture was precipitated in 20:1 molar excess of demi-water and the milky mixture was then centrifuged.

The watery phase was then decanted and the solid product was dried in the oven at 150 °C overnight to remove any traces of water and unreacted cyclopentadiene. The resulting polymer was ground and then obtained as a dark brown powder. Solubility in several aprotic solvent (i.e. DMSO, chlorinated hydrocarbons, DMF) was visually tested.

Through the elemental analysis of the polymer, the nitrogen content can be correlated with the fraction (z) cyclopentadiene groups via equation 2:

\[
N(\%) = \frac{M_N \cdot nN_y \cdot y + M_N \cdot nN_z \cdot z}{M_{wx} \cdot x + M_{wy} \cdot y + M_{wz} \cdot z}
\]

Where \(M_N\) is the atomic mass of nitrogen, \(nN_x\) and \(nN_y\) are the number of nitrogen in the \(x\) and \(y\) repetitive units (\(V\) in Figure 4.1), \(x\), \(y\) and \(z\) are the fraction of the respective repetitive units, while \(M_{wx}\), \(M_{wy}\) and \(M_{wz}\) are the molecular weight of the respective repetitive units calculated by considering the ratio ethene/propane.

By solving the two equations 1 and 2, together with the mass balance on the converted carbonyl units \((y+z=\text{conv as calculated in equation 1})\), \(y\) can be calculated according to equation 3:

\[
y = \frac{N \cdot (M_{wx} \cdot x + 0.55 \cdot M_{wz}) - M_N \cdot nN_z \cdot 0.55}{M_N \cdot (nN_y - nN_z) - N \cdot (M_{wy} - M_{wz})}
\]

Based on this, PKCPD1 showed 9.0 % of the 1,4-di-carbonyl repetitive units converted to cyclopentadienyl functionalized pyrroles while PKCPD2 gave a conversion of 21.7 %. The most relevant data from the characterization are reported below.

EA (PKCPD1): Calcd. C 68.07; H 7.98; Cl 9.13; N 4.51; O 10.30 Found C 67.86; H 7.80; Cl 9.05; N 4.51; O 10.78
EA (PKCPD2): Calcd. C 69.50; H 8.01; Cl 8.25; N 4.66; O 9.58 Found C 69.25; H 8.05; Cl, 8.36; N, 4.66; O 9.68
FT-IR (PKCPD1 and PKCPD2): 787 (ring bending cyclopentadiene dimer); 1408 (C-H CPD bending); 1538 (C=C CPD dimer stretching); 1625 (C=C CPD stretching); 3088 (C-H CPD stretching).

4.2.6 Gelation experiment

The gelation test was carried out in a 4 ml sample vial. PKCPD2 was dissolved in DMSO by previously warming the solvent up to 160 °C. After that, the DA cross-linking reaction was carried out by cooling to 30°C overnight. The resulting gel was then heated at 160 °C again for an hour in order to de-cross-link once again the network.
4.3 Results and discussion

4.3.1 Frontier molecular orbital (FMO) calculation

The temperature at which the DA adduct is formed as well as the one at which it is broken are key parameters in determining the thermal behavior of a reversible thermoset based on the DA-rDA mechanism. Both temperatures are in principle dependent on the kind of DA groups used for the cross-linking reaction and the chemical structure of the polymeric matrix [31]. The idea to use cyclopentadienyl groups instead of furan-maleimide ones on a polyketone backbone, although based on previous work on similar systems [25], can be easily checked from a theoretical point of view by taking into account the free energy of the corresponding DA and rDA reactions. For both systems, the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) energies were determined through frontier molecular orbital (FMO) calculations. Such technique proved to be the most suitable for theoretical consideration about orbital energy levels [32].

Since the Diels-Alder reaction mechanism involves the transfer of an electron couple from the HOMO of the diene to the LUMO of the dienophile (ΔE), a relatively high energy difference between these molecular orbitals would correlate with a high activation barrier for the reaction. An higher activation barrier for the direct reaction corresponds to higher Diels-Alder temperature values. The same is true for the retro Diels Alder, with higher activation barrier corresponding to higher retro Diels-Alder temperature values [33].

The calculations (Table 4.1) showed indeed a higher activation energy for the Diels-Alder formation with furan-maleimide system while cyclopentadiene units displayed the highest energy barrier for the reverse reaction.

<table>
<thead>
<tr>
<th>Diels-Alder system</th>
<th>ΔE [eV]a</th>
<th>ΔE' [eV]b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furan/Bis-maleimide</td>
<td>58.90</td>
<td>18.12</td>
</tr>
<tr>
<td>Cyclopentadiene/Cyclopentadiene</td>
<td>14.27</td>
<td>22.59</td>
</tr>
</tbody>
</table>

Table 4.1 HOMO - LUMO energy gaps, for Diels-Alder reactions calculated by Ab-Initio simulation; a) Energy gap between HOMO of Diene and LUMO Dienophile, b) Energy gap between HOMO of adduct and LUMO of adduct.

Thus the retro-Diels-Alder of cyclopentadiene should occur at higher temperatures than furan-maleimide system. This is particularly interesting in order to build up thermo-reversible thermosets that can operate at relatively high temperatures.
Endo and exo stereo-isomers

The Diels-Alder cycloaddition reaction can yield two diastereoisomers. Indeed, orbital overlapping of the two reacting molecules will occur only with the electrons of HOMO from one component and the LUMO vacant orbital from the other one. The diene and the dienophile couple can approach each other in two ways, which both allow overlapping of the involved orbitals and result in the formation of two stereoisomers structures, the endo and exo adducts.

One of these interactions results in an exo-product, in which the remaining double bonds point away from each other and one in an endo-product in which the double bonds point towards each other. The endo product contains additional secondary orbital interactions, which strengthen the bonding of this product with respect to the exo-product [34]. As a consequence, the endo-isomer is kinetically favored, while the exo-isomer is thermodinamically favored. This can be shown by comparing the reaction enthalpies of the two reactions, calculated through FMO calculations. By using the Hess' law, the reaction enthalpies for the propyl-cyclopentadiene dimer were calculated as listed in Table 4.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>$H^r$ [kcal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Endo-adduct</td>
<td>-20.3</td>
</tr>
<tr>
<td>Exo-adduct</td>
<td>-21.6</td>
</tr>
</tbody>
</table>

Table 4.2 Reaction enthalpies ($H^r$) for Diels-Alder reaction towards two diastereoisomers of propyl-cyclopentadiene.

As can be seen, the reaction to the exo-adduct is more exothermic than the reaction to the endo-adduct. Therefore, higher temperatures favor the dissociation of the exo-adduct over the endo-adduct. This explains the selectivity for the endo- or exo-adduct at different temperatures, and specifically favors the endo-reaction at low reaction temperatures.

The study of such phenomenon might be a key in tuning (i.e. by varying the relative exo/endo ratio) the material stability by modifying processing parameters, such as temperature gradient for cross-linking in molding process.

4.3.2 Synthesis of cyclopentadiene functionalized polyketones

Synthesis of PKCl

The first step towards the attachement of cyclopentadiene units to the polyketone backbone is the Paal-Knorr reaction of aminopropyl chloride with 1,4 dicarbonyls groups along the polymer backbone. Calculations based on the elemental analysis of the product showed that 55 % of the 1,4-dicarbonyl groups were converted.
This process of aromatization of the backbone through the formation of pyrrole rings is well documented in previous publications by our group [25, 35]. The functionalization of the polymer is confirmed by specific NMR signals for the pyrrole and for the grafted functional group (vide supra). Indeed, from $^1\text{H}$-NMR measurements (Figure 4.2), a broad band centered at 5.45-5.95 ppm (pyrrolic hydrogens) appears in the spectrum of PKCl and, together with the signal at 3.50 ppm (methylene in $\alpha$-position to the chloride) and at 3.87 ppm (methylene in $\alpha$-position to the pyrrole), confirmed the structure of the polymer.

![Figure 4.2 $^1\text{H}$-NMR spectra of PK50 and the chlorine modified polyketone (PKCl).](image)

Moreover, the appearance of FT-IR signals (not shown for brevity) at 667 and 749 cm$^{-1}$, i.e. bending and stretching of C-Cl respectively [36], and at 1039 and 1375 cm$^{-1}$, i.e. C-H in plane deformation and C-N pyrrole ring stretch [37], further highlight the spectroscopic differences with respect to the unmodified polyketone.

**Synthesis of PKCPD**
The chlorinated polyketone was reacted with lithium cyclopentadiene to form the cyclopentadiene-functionalized polymer (Figure 4.1). The cyclopentadiene conversion of the two obtained polymers (i.e. PKCPD1 and PKCPD2) was calculated through elemental analysis of the purified product, yielding values of 9 % for PKCPD1 and 22 % for PKCPD2 with the respect to the initial 1,4-dicarbonyl groups.

An attempt to characterize the reaction with $^1\text{H}$-NMR was unsuccessful. The reason for this was the insolubility of the reaction product at temperatures below 160°C, probably as a result of partial DA cross-linking already at room temperature. ATR FT-IR studies of the insoluble materials could be performed in order to assess the cross-linking structure of the thermoset.
The spectra of chlorinated polyketone (PKCl) and cyclopentadiene functionalized polyketone (PKCPD) are shown in Figure 4.2.

The most notable differences between the spectra of PKCl and PKCPD1 are the appearance of new peaks at 3088 cm$^{-1}$ and a broadening of the peak at 1625 cm$^{-1}$ and at 787 cm$^{-1}$. Peaks at 1610 cm$^{-1}$ and 1640 cm$^{-1}$ were assigned to dicyclopentadiene by Akhmedov and Isakov [38]. They were also observed by Chen and Ruckenstein [27] at 1633 cm$^{-1}$ and 1601 cm$^{-1}$ respectively as well as by Peng et al. [39] at 1610 cm$^{-1}$ and 1580 cm$^{-1}$ respectively. Peng et al. further explain that the peak at 1610 cm$^{-1}$ is attributed to the cyclopentadienic double bond and the peak at 1580 cm$^{-1}$ to the norbornenic double bond. Long et al. [40] observed adsorption peaks at 3100 cm$^{-1}$ and 1408 cm$^{-1}$ for dicyclopentadiene C-H stretching and C=C respectively. The first absorption explains the new peak at 3088 cm$^{-1}$. The mentioned peak at 1408 cm$^{-1}$ is also present in PKCPD (although it overlaps with a larger peak that was also present in PKCl), thus suggesting the cyclopentadiene anchoring to the polyketone backbone. Chen and Ruckenstein also explained the formation of a peak at 790 cm$^{-1}$, assigned to the ring bending of the cyclopentadiene dimer, which is also present in our case at 787 cm$^{-1}$. Since the peak at 1700 cm$^{-1}$ can be assigned to the carbonyl groups stretching and the latter does not decrease after reaction with cyclopentadienyl lithium, it can be stated, at least within the detection limit of the FT-IR, that the carbonyl are not involved in the reaction with cyclopentadienyl lithium (Figure 4.1).

From these results, it can be concluded that the functionalization of cyclopentadiene on PKCl was successful, according to the proposed chemical mechanism.
4.3.3 Self-cross-linking gelation of PKCPD1

A simple gelation test was carried out in order to check the self-reversible behavior of PKCPD1 (Figure 4.3). The latter is dissolved in DMSO and de-cross-linked at 160 °C (Figure 4.3 a). The DA cross-linking reaction has been carried out over night at 30 °C. The resulting gel (Figure 4.3 b) was then heated at 160 °C again for an hour (Figure 4.3 c).

![Gelation experiment](image)

**Figure 4.3** Gelation experiment: A) initial state of PKCPD1 (dissolution at 160 °C in DMSO); B) gel formation (overnight at 30 °C); C) solution at 160 °C in DMSO.

Thus thermo-reversibility of PKCPD1 is clearly indicated here. These results are in agreement with what observed by Chen and Ruckenstein [27], who found, for a similar system, a sharp reduction in viscosity (taken as indication of thermal reversibility) in the range of 150-170 °C. Moreover, other authors [41-43] determined the same de-cross-linking temperature values (i.e. around 150 °C) for monomeric units of dicyclopentadienyls linked by ester moieties.

4.3.4 Thermo-mechanical properties of the thermosets

In order to understand the thermal behavior during material re-processing cycles, DSC measurements were carried out for six consecutive thermal cycles. DSC measurements of PKCPD1 (normalized data in Figure 4.4) showed a broad exothermic transition from 75-100 °C till 180 °C (related to the rDA reaction) and a second-order transition (i.e. T_g of the polymer backbone) around 65-67 °C.
The broad endothermic peak shifts at slightly higher temperature values with the number of thermal cycles performed (Table 4.3). This is in agreement to what observed for cyclic dicyclopentadienyl connected through ester bonds to aliphatic spacers [41-43]. In particular, a study [42] showed that the rDA exothermal peak is dependent on the heating rate (i.e. from 2 °C/min till 15 °C/min) with a clear shift towards higher temperatures (in the range 190-210 °C) for measurements performed at lower heating rates. Shifts towards the upper range limit or even the appearance of shoulders in the DSC can be related to the formation of trimers of cyclopentadiene [28]. In the present case, the upper range of the endothermic peak (180 °C) suggests the possible formation of multimeric cyclopentadienyl structures.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>Heat generated</th>
<th></th>
<th></th>
<th>T_{rDA} PKCPD1 (°C)</th>
<th>T_{rDA} PKCPD2 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PKCPD1</td>
<td>PKCPD2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Absolute value (J/g)</td>
<td>loss percentage</td>
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<td>loss percentage</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.98</td>
<td>N/A</td>
<td>1.29</td>
<td>N/A</td>
<td>132</td>
</tr>
<tr>
<td>2</td>
<td>0.82</td>
<td>16.3%</td>
<td>0.98</td>
<td>23.6%</td>
<td>135</td>
</tr>
<tr>
<td>3</td>
<td>0.70</td>
<td>14.1%</td>
<td>0.77</td>
<td>21.2%</td>
<td>134</td>
</tr>
<tr>
<td>4</td>
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<td>13.8%</td>
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<td>15.2%</td>
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</tr>
<tr>
<td>5</td>
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<td>13.1%</td>
<td>0.59</td>
<td>10.7%</td>
<td>139</td>
</tr>
<tr>
<td>6</td>
<td>0.43</td>
<td>19.4%</td>
<td>0.47</td>
<td>20.4%</td>
<td>140</td>
</tr>
</tbody>
</table>

Table 4.3 Integral values and heat loss (compared to the previous cycle) in percentage for six cycles of PKCPD1 and PKCPD2 and the respective rDA temperatures.

Moreover, the rDA temperature slightly increased upon heating/cooling (i.e. for every thermal cycle) and its integral follow the opposite trend (Table 4.3). The latter was already observed in the previous work of our
The decrease in the rDA DSC integrals of cyclopentadiene may be related to the presence of different trimer/dimer units ratio (Figure 4.1) or simply loss of thermo-recovery efficiency. Indeed, trimers of cyclopentadienyl display a different rDA temperature than dicyclopentadienyl units [42]. The same considerations outlined above are actually valid for DSC measurements of the higher conversion cyclopentadiene polymer (PKCPD2) (Figure 4.5).

Figure 4.5 Normalized DSC scans of PKCPD2, 6 scans.

PKCPD2 showed the same DSC profile as PKCPD1, but, as expected on the basis of the chemical composition, larger integral values of the rDA exotherm are observed (Table 4.3). Moreover, all six peaks for the PKCPD2 rDA reaction slightly shifted towards higher temperatures values when compared to PKCPD1 ones (Table 4.3). This phenomenon was already observed in our previous studies when thermosets with higher furan density displayed higher T_{rDA} in the presence of an aromatic bismaleimide [25]. It is most probably related to a change in the relative amount of exo and endo adducts. This behavior is particularly interesting as a tool to simply tune the rDA temperature by an increase in the degree of cyclopentadiene functionality on the modified polymer.

DMTA analyses were carried out in order to test the thermo-mechanic reversibility of PKCPD1. The DMTA profile (Figure 4.6) shows a maximum tan (δ) at 203 °C, which shifts at higher temperature values (i.e. till 209 °C) with the number of thermo-mechanical cycles performed. Particularly striking is the fact that up to 6 cycles were performed without any negligible loss in storage modulus.
Figure 4.6 DMTA measurements of PKCPD1

The peak of tan (δ) at 209 °C cannot be interpreted as glass transition temperature of the material since it is already observed during DSC measurements around 65-67 °C. The profile of the storage modulus resembles the DMTA profile of a cross-linked elastomer, thus suggesting that this softening temperature might be related to the breakage of the cross-linking points. Indeed, the same was observed for a thermo-reversible furan-maleimide elastomer by N. Teramoto et al. [44]. By using a difurfurylidene trehalose and maleimide-terminated oligo(dimethylsiloxane), they observed in DMTA analysis a sharp decrease at -108 °C, which was the glass transition of the material. However, the storage modulus did not vary till the beginning of the rDA reaction at 100°C. Indeed, at that point, de-polymerization and loss of mechanical properties are observed.
4.4 Conclusions

Thermally recyclable thermosets based on the Diels-Alder cyclo-addition of cyclopentadiene were synthesized according to a novel two-step procedure starting from aliphatic polyketones. The latter were modified through the Paal-Knorr reaction to obtain chlorine moieties linked to pyrrolic units along the polyketone backbone. These were subsequently reacted with cyclopentadienyl lithium to obtain cyclopentadiene-functionalized polymers.

The thermoreversibility of the materials was proven by gelation experiments, DSC and DMTA analysis. DSC measurements showed a broad rDA exothermic transition around 70-180 °C assigned to dicyclopentadiene rDA de-cross-linking. On the other hand, the material start to soften around 200-210 °C as observed in DMTA measurements and it can be recycled without any significant loss in mechanical properties up to six cycles. Such outstanding thermal stability can be preliminary explained, on the basis of similar systems described in the literature, by the formation of higher aggregates (e.g. trimers of cyclopentadiene). In the present case, multi-functional cross-linking points would hold the network. Independently of the exact mechanism, it must be stressed how a remarkable improvement of the thermo-reversible thermoset application window is attained.
4.5 References

[42] Park, J.S.; Takahashi, K; Guo, Z.; Wang, Y; Bolanos, E.; Hamann-Schaffner, C.; Murphy, E.; Wudl, F. *J. of Comp.Mat.* **2008**, 42, 26, 2869.