

Cyclopentadiene-functionalized polyketone as self-cross-linking thermo-reversible thermoset with increased softening temperature

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ABSTRACT: Self-cross-linkable thermo-reversible thermosets were obtained by a two-steps post-functionalization of aliphatic alternating polyketones yielding two different cyclopentadiene functionalization degree of 9 and 22% (with the respect of initial 1,4-dicarbonyl units). Thermo-reversibility was verified by gelation experiments and differential scanning calorimetry (DSC) scans displayed a broad transition varying from 75–100°C till 160°C that can be related to retro-Diels Alder de-bonding of the dicyclopentadienyl moieties. The dynamic mechanical thermal (DMTA) analysis showed the complete thermo-mechanical recovery of the material up to six thermal cycles with a softening temperature around 210°C, thereby ensuring a suitable application window for high-temperature resistant thermosets. Independently of the exact mechanism at the molecular level and in addition to previous studies which used the same Diels-Alder diene-dienophile system, it must be noticed that all prepared materials retained their mechanical behavior during at least six consecutive thermal cycles, thus indicating the re-workability of the system. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42924.

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INTRODUCTION

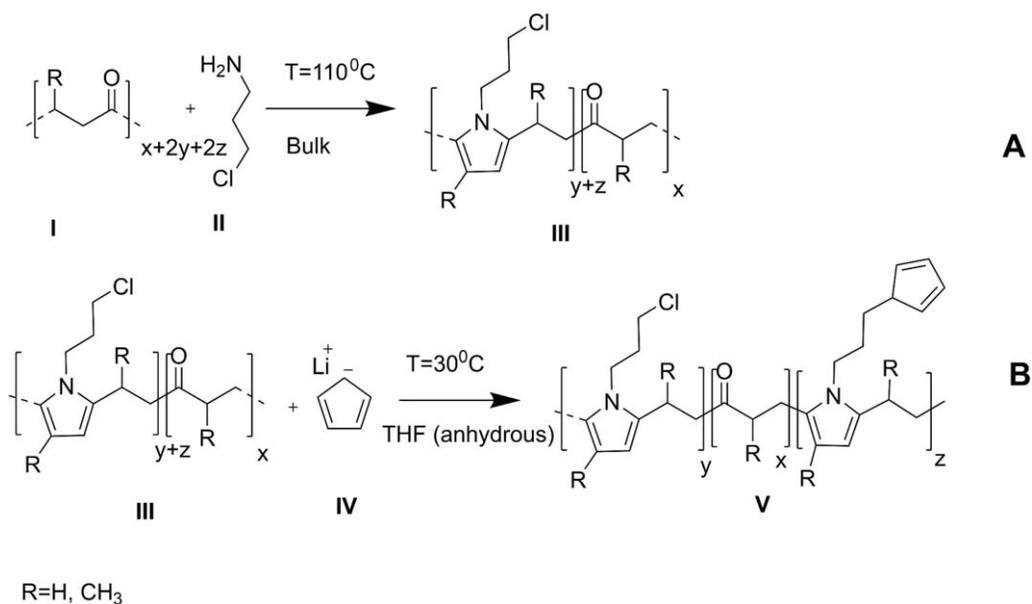
Thermosetting polymers differ from thermoplastics due to the formation of a 3-dimensional network of covalent intermolecular bonds. The latter creates a rigid network¹ that translates into relatively high creep resistance, high modulus, dimensional stability at high temperatures and chemical resistance.² 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, these materials are difficult to re-process without initiating their degradation, which ultimately leads to irreversible deterioration of the mechanical behavior.⁵ One possible approach towards fully recyclable thermosets is the use of reversible cross-linking points that undergo de-cross-linking without undermining the integrity of the backbone structure.⁶ An external stimulus, such as pH, light,⁷ or heat may be utilized for the selective scission of the cross-linking bridges. The reversible cross-linking might consist of non-covalent interaction, e.g., hydrogen bonds^{8,9} and ionic¹⁰ 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 promising candidate¹³ 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



Scheme 1. Two step synthesis pathway of cyclopentadiene-modified polyketones.

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 or 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 dynamic mechanical thermal analysis, DMTA) of the corresponding reversible network as well as, to some extent, the de-cross-linking one (as determined by differential scanning calorimetry, 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. Albeit different diene-dienophile has been investigated in order to increase the rDA temperature (i.e., anthracene-maleimide²⁶), only the cyclopentadiene-based DA/rDA chemistry provides a thermo-reversible system displaying a higher softening temperature with limited polymer degradation, as it is shown by Kennedy and Castner²⁷ and subsequently Chen and Ruckenstein.²⁸ In the first case, the authors carried out a reaction between dicarboxylate di-cyclopentadienyl 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 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. This is further confirmed by a recent study where the authors found out through torque measurements that this thermo-reversible network has an ideal temperature of 174°C for re-processability with limited side-reaction and acceptable flowability.²⁹

In 2008, Murphy *et al.*³⁰ revised an old system invented by J.K. Stille and L. Plummer³¹ to synthesize a dicyclopentadiene connected cyclically by aliphatic ester bridges. This work 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.*³⁰ 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 aimed at combining the peculiar multimer Diels-Alder cross-linking approach which ensures a softening temperature suitable for high-temperature thermosets^{28,30} applications with the same polymer platform that has already shown excellent mechanical stability during thermo-reversibility cycles²⁵ (Scheme 1).

The synthesis of the chloride functional polymer (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 ¹H-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 Fourier-transformed infrared (FT-IR) studies and elemental analysis (EA) calculation.

Furthermore, the thermal reversibility is tested and analyzed by differential scanning calorimetry measurements and gelation experiments while the thermo-mechanical properties of the obtained thermosets are determined by dynamic mechanical thermal analysis.

EXPERIMENTAL

Materials

The alternating polyketones, ter-polymers 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.³² 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.

Physico-Chemical Characterization

$^1\text{H-NMR}$ spectra were recorded on a Varian Mercury Plus 400 MHz apparatus. CDCl_3 was used as the solvent. Fourier-transformed infrared (FT-IR) spectra were recorded using a Perkin-Elmer Spectrum 2000 equipped with a heating stage and temperature controller. Differential Scanning Calorimetry (DSC) analysis was performed using a Perkin-Elmer differential scanning calorimeter Pyris 1 under N_2 atmosphere from 20 to 180°C at a rate of 10°C per minute. Elemental analysis was performed using a Euro EA elemental analyzer. Dynamic mechanical thermal analysis (DMTA) 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. Samples were 5.8 mm wide, 1.3 mm thick, and 54 mm long. These sample bars were pressed for 20 min 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 six consecutive cycles between room and softening temperature.

Procedures

Synthesis of modified aliphatic polyketones with chlorine pendant groups. 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 h 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 gas chromatography equipped with mass spectrometry (GC/MS) in order

to check when the product was well purified). The product was then filtered and freeze-dried for 24 h. The reaction yielded a light brown product (PKCl).

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 11.76; N 4.53; O 11.93.

$^1\text{H-NMR}$ (CD_3Cl): 1.04 ($\text{CH}_3\text{-CH}$ aliph.); 1.83 ($\text{CH}_3\text{-CH}$ arom.); 1.94 ($\text{Cl-CH}_2\text{-CH}_2$); 2.2-3.1 (CH_2 aliph.); 3.50 ($\text{CH}_2\text{-Cl}$); 3.87 (N-CH_2); 5.45-5.95 (CH arom.)

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

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 N_2 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 at relatively high temperatures (i.e., above 160°C).

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 cm^{-1} (ring bending CPD dimer); 1408 cm^{-1} (C-H CPD bending); 1538 cm^{-1} (C=C CPD dimer stretching); 1625 cm^{-1} (C=C CPD stretching); 3088 cm^{-1} (C-H CPD stretching).

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.

Calculation of PKCl functionalization degree by elemental analysis. The carbonyl conversion was calculated on the basis of the nitrogen content of the final product (N) according to the following formula:

$$\text{Conv} = \frac{[(N \cdot 0.01)/14 \cdot n] \cdot PK(g)}{PK(g)/M_{PK} - PK(g)/M_{PK} \cdot M_{Amine} \cdot [(N \cdot 0.01)/14 \cdot n] + 2 \cdot PK(g)/M_{PK} \cdot M_{Water} \cdot [(N \cdot 0.01)/14 \cdot n]} \quad (1)$$

where M_{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_{Water} and M_{Amine} are the molecular weight of water and the amine compound, respectively. **PKCl** showed a carbonyl conversion of 55.0%.

Calculation of cyclopentadiene functionalization degree in PKCPD1 and PKCPD2 by elemental analysis. Through the elemental analysis of the polymer, the nitrogen content can be correlated with the fraction (z) cyclopentadiene groups via eq. (2):

$$N(\%) = \frac{M_N \cdot nN_y \cdot y + M_N \cdot nN_z \cdot z}{M_{wx} \cdot x + M_{wy} \cdot y + M_{wz} \cdot z} \quad (2)$$

Where M_N is the atomic mass of nitrogen, nN_y and nN_z are the number of nitrogen in the x and y repetitive units (**V** in Scheme 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/propene.

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

$$y = \frac{N \cdot (M_{wx} \cdot x + 0.55 \cdot M_{wz}) - M_N \cdot nN_z \cdot 0.55}{M_N \cdot (nN_y - nN_z) - N \cdot (M_{wy} - M_{wz})} \quad (3)$$

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%.

Frontier molecular orbital (FMO) calculations. Frontier molecular orbital (FMO) calculations were performed with HyperChem Release 8.0. The molecular orbital energy levels were calculated based on a simulation that uses an *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.

RESULTS AND DISCUSSION

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.³³ 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.³⁴

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 directly correlate with the activation energy for the reaction. This for the direct reaction would correspond to the need of higher temperature in order to kinetically observe the occurring of the reaction.

The same is true for the retro Diels Alder, with higher activation barrier hindering the occurring of the retro Diels-Alder at lower temperature range.³⁵

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

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.

Synthesis of Cyclopentadiene Functionalized Polyketones

Synthesis of PKCl. The first step towards the anchoring of cyclopentadiene units to the polyketone backbone is the Paal-Knorr reaction of aminopropyl chloride with 1,4-dicarbonyl groups along the polymer backbone. Calculations based on 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.^{25,36} The functionalization of the polymer is confirmed by specific NMR signals for the pyrrole and for the grafted functional group (*vide supra*). Indeed, from ¹H-NMR measurements (Figure 1), 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 α -

Table I. HOMO - LUMO Energy Gaps, for Diels-Alder Reactions Calculated by *Ab-Initio* Simulation

Diels-Alder system	ΔE [eV] ^a	$\Delta E'$ [eV] ^b
Furan/Bis-maleimide	58.90	18.12
Cyclopentadiene/Cyclopentadiene	14.27	22.59

^a Energy gap between HOMO of diene and LUMO of dienophile.

^b Energy gap between HOMO of adduct and LUMO of dienophile.

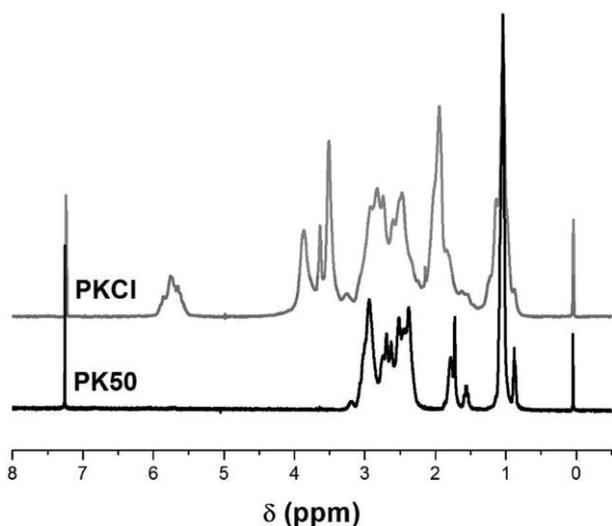


Figure 1. $^1\text{H-NMR}$ spectra of alternatic aliphatic polyketone with 50% ethene and 50% propene content (**PK50**) and the chlorine modified polyketone (**PKCl**).

position to the chloride) and at 3.87 ppm (methylene in α -position to the pyrrole), confirmed the polymer structure.

Moreover, the appearance of FT-IR signals (not shown for brevity) at 667 and 749 cm^{-1} , that is, bending and stretching of C-Cl respectively,³⁷ and at 1032 and 1375 cm^{-1} , that is, C-H in plane deformation and C-N pyrrole ring stretch,³⁸ further highlight the spectroscopic differences with respect to the unmodified polyketone.

Synthesis of PKCPD. The chlorinated polyketone (**PKCl**) underwent a nucleophilic substitution reaction with lithium cyclopentadiene to yield the cyclopentadiene-functionalized polymer (Scheme 1). The cyclopentadiene conversion of the two obtained polymers (i.e., **PKCPD1** and **PKCPD2**) was calculated through elemental analysis of the purified product, reaching 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 behind this was the insolubility of the

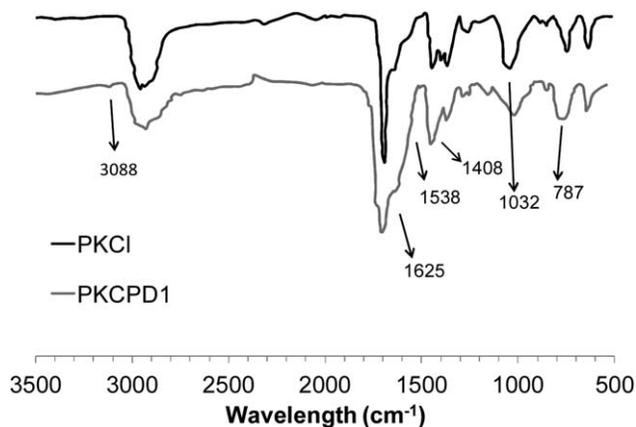


Figure 2. FT-IR scans of chlorine modified polyketone (**PKCl**) and cyclopentadiene functionalized polyketone (**PKCPD1**).

reaction product at temperatures below 160°C, probably as a result of partial DA bonding occurring 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 2.

The most notable differences between the spectra of **PKCl** and **PKCPD1** are the broadening of the peak at 1625 cm^{-1} and at 787 cm^{-1} . Peaks at 1633 cm^{-1} and 1601 cm^{-1} have already been detected in previous works^{28,39} and has been assigned to the cyclopentadienic double bond and the norbornenic double bond. The same authors also explained the formation of a peak at 790 cm^{-1} as related to the ring bending of the cyclopentadiene dimer.

Furthermore, Long *et al.*⁴⁰ noticed absorption peaks at 3100 cm^{-1} and 1408 cm^{-1} assigned to dicyclopentadiene C-H stretching and C=C respectively. While the first one is clearly visible, the latter at 1408 cm^{-1} appeared as a shoulder of a larger peak that was already present in **PKCl**. 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 (Scheme 1). From these results, it can be concluded that the functionalization of cyclopentadiene on **PKCl** was successful, according to the proposed chemical mechanism.

Self-cross-linking gelation of PKCPD1

A simple gelation test was carried out in order to check the self-reversible behavior of **PKCPD1** (Figure 3). The material was dissolved in DMSO and de-cross-linked at 160°C [Figure 3 (a)]. The DA cross-linking reaction has been carried out overnight at 30°C. The resulting gel [Figure 3(b)] was then heated at 160°C again for an hour [Figure 3(c)].

Thus, thermo-reversibility of **PKCPD1** is clearly indicated here. These results are in agreement with what observed by X. Chen and E. Ruckenstein,²⁸ 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 di-cyclopentadienyls linked by ester moieties. Recently, a study⁴⁴ showed that, by submerging the cross-linked network in toluene for 14 h, the

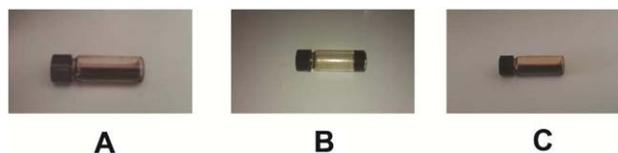


Figure 3. Gelation experiment: (A) initial state of **PKCPD1** (dissolution at 160°C in DMSO); (B) gel formation (overnight at 30°C); (C) solution at 160°C after one hour in DMSO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

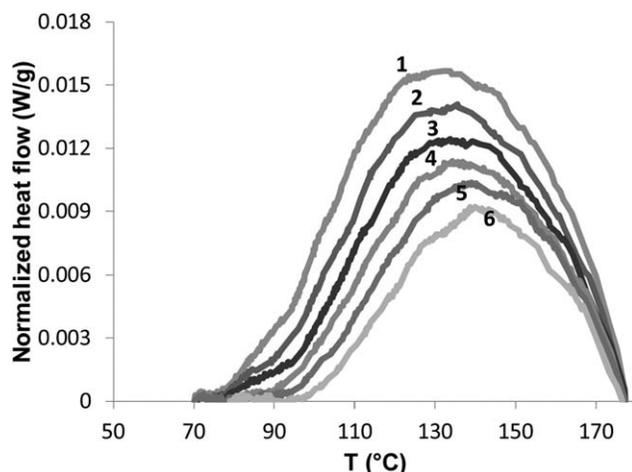


Figure 4. Normalized DSC insert on rDA exothermal peak for PK-CPD1 (9.0% cyclopentadiene conversion with respect to 1,4-dicarbonyl groups) during six consecutive thermal cycles (heating rate $10^{\circ}\text{C min}^{-1}$ under N_2).

detaching of the dicyclopentadiene units can occur at temperatures as low as 90°C .

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) showed a broad exothermic transition from $75\text{--}100^{\circ}\text{C}$ till 180°C (related to the rDA reaction) and a second-order transition (i.e., T_g of the polymer backbone) around $65\text{--}67^{\circ}\text{C}$.

The broad endothermic peak shifts at slightly higher temperature values with the number of thermal cycles performed (Table II). This is in agreement to what observed for cyclic dicyclopentadienyl connected through ester bonds to aliphatic spacers.^{42,43}

In particular, a study⁴¹ showed that the rDA exothermal peak is dependent on the heating rate (i.e., from $2^{\circ}\text{C min}^{-1}$ till $15^{\circ}\text{C min}^{-1}$) with a clear shift towards higher temperatures (in the range $190\text{--}210^{\circ}\text{C}$) for measurements performed at lower heating rates. Shifts towards the upper range limit or even the appear-

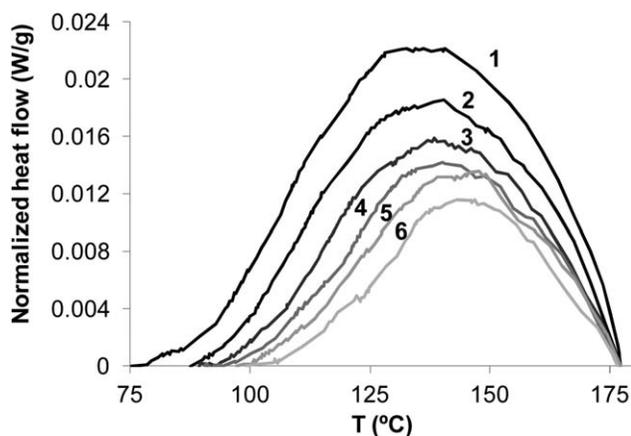


Figure 5. Normalized DSC insert on rDA exothermal peak for PK-CPD2 (22.0% cyclopentadiene conversion with respect to 1,4-dicarbonyl groups) during six consecutive thermal cycles (heating rate $10^{\circ}\text{C min}^{-1}$ under N_2).

ance of shoulders in the DSC can be related to the formation of trimers of cyclopentadiene.³⁰ In the present case, the upper range of the endothermic peak (180°C) suggests the possible formation of multimeric cyclopentadienyl structures.

Moreover, the rDA temperature slightly increased upon heating/cooling (i.e. for every thermal cycle) and its integral follow the opposite trend (Table II). The latter was already observed in the previous work of our group.²⁵ The decrease in the rDA DSC integrals of cyclopentadiene may be related to the presence of different trimer/dimer units ratio (Scheme 1) or simply loss of thermo-recovery efficiency. Indeed, trimers of cyclopentadienyl display a different rDA temperature than dicyclopentadienyl units.⁴¹ The same considerations outlined above are actually valid for DSC measurements of the higher conversion cyclopentadiene polymer (PKCPD2) (Figure 5).

PKCPD2 showed the same DSC profile as PKCPD1, but, as expected on the basis of the chemical composition, larger integral values of the rDA exothermic peaks are observed (Table II). Moreover, all six peaks for the PKCPD2 rDA reaction slightly shifted towards higher temperatures values when compared to

Table II. Integral Values and Heat Loss (Compared to the Previous Cycle) in Percentage for Six Cycles of PKCPD1 and PKCPD2 and the Respective rDA Temperatures

Cycle number	Heat generated				$T_{\text{rDA}}\text{PKCPD1 } (^{\circ}\text{C})$	$T_{\text{rDA}}\text{PKCPD2 } (^{\circ}\text{C})$
	PKCPD1		PKCPD2			
	Absolute value (J g^{-1})	Loss percentage	Absolute value (J g^{-1})	Loss percentage		
1	0.98	N/A	1.29	^a	132	133
2	0.82	16.3%	0.98	23.6%	135	140
3	0.70	14.1%	0.77	21.2%	134	138
4	0.61	13.8%	0.66	15.2%	134	140
5	0.53	13.1%	0.59	10.7%	139	148
6	0.43	19.4%	0.47	20.4%	140	143

^aNot applicable.

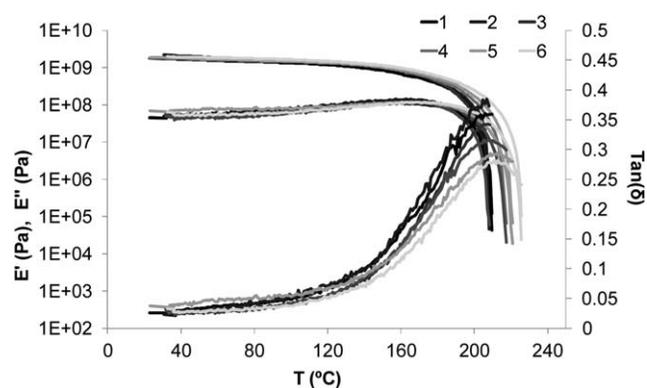


Figure 6. DMTA measurements of PKCPD1 (9.0% cyclopentadiene conversion with respect to 1,4-dicarbonyl groups) during six consecutive thermal cycles (heating rate $3^{\circ}\text{C min}^{-1}$).

PKCPD1 ones (Table II). 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 in order to optimize the temperature range of DA/rDA according to the required thermoset application window 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 6) shows a maximum $\tan(\delta)$ at 203°C , which shifts at higher temperature values (i.e., till 209°C) with consecutive thermo-mechanical cycles performed. Particularly striking is the fact that up to six cycles were performed without any negligible loss in storage modulus. Moreover, the slight toughening of the thermoset network, as shown by the increased storage modulus values with the number of thermal cycles, has already been observed by E. Murphy⁴⁵ for cyclic dicyclopentadienyl connected through ester bonds to ethylene glycol spacers by employing a lower softening temperature (i.e., 175°C for 5 min).

The peak of $\tan(\delta)$ at 209°C cannot be interpreted as glass transition temperature of the material since it is already observed during DSC measurements around $65\text{--}67^{\circ}\text{C}$. 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 Teramoto *et al.*⁴⁶ 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.

CONCLUSIONS

Thermally recyclable thermosets based on the Diels-Alder cycloaddition 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 verified by gelation experiments, DSC and DMTA analysis. DSC measurements showed a broad rDA exothermic transition around $70\text{--}180^{\circ}\text{C}$ assigned to di-cyclopentadiene rDA de-cross-linking. On the other hand, the material starts to soften around $200\text{--}210^{\circ}\text{C}$ 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 preliminarily 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 with a thermally stable polymer platform which keeps unaltered the thermoset mechanical properties throughout all the thermal cycles investigated.

REFERENCES

- Trotignon, J. P.; Verdu, J.; Martin, C.; Morel, E. *J. Mater. Sci.* **1993**, *28*, 2207.
- Sperlin, L. H.; Mishra, V. *Polym. Adv. Technol.* **1995**, *7*, 197.
- Pickering, S. J. *Compos. Part A: Appl. Sci. Manuf.* **2006**, *37*, 1206.
- Derosa, R. J. *Thermoplast. Compos. Mater.* **2005**, *18*, 219.
- Adhikari, B. *Prog. Polym. Sci.* **2000**, *25*, 909.
- Leibler, L.; Rubinstein, M.; Colby, R. H. *Macromolecules* **1991**, *24*, 4701.
- Suzuki, T.; Shinkai, S.; Sada, K. *Adv. Mater.* **2006**, *18*, 1043.
- Nair, K. P.; Breedveld, V.; Weck, M. *Macromolecules* **2008**, *41*, 3429.
- Peng, C. C.; Abetz, V. *Macromolecules* **2005**, *38*, 5575.
- Hennink, W.; van Nostrum, C. *Adv. Drug Deliv. Rev.* **2002**, *54*, 13.
- Liu, C.; Qin, H.; Mather, P. T. *J. Mater. Chem.* **2007**, *17*, 1543.
- Cordier, P.; Tournilhac, F.; Soulié-Ziakovic, C.; Leibler, L. *Nature* **2008**, *451*, 977.
- Kwart, H.; King, K. *Chem. Rev.* **1968**, *68*, 415.
- Watanabe, M.; Yoshie, N. *Polymer (Guildf)* **2006**, *47*, 4946.
- Bergman, S. D.; Wudl, F. *J. Mater. Chem.* **2008**, *18*, 41.
- Chen, X.; Dam, M.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. *Science* **2002**, *295*, 1698.
- Luo, J.; Haller, M.; Li, H.; Kim, T. D.; Jen, A. K. Y. *Adv. Mater.* **2003**, *15*, 1635.

18. Canary, S. A.; Stevens, M. P. *J. Polym. Sci. Part A: Polym. Chem.* **1992**, *30*, 1755.
19. Stevens, M. P.; Jenkins, A. D. *J. Polym. Sci. Polym. Chem. Ed.* **1979**, *17*, 3675.
20. Goussé, C.; Gandini, A.; Hodge, P. *Macromolecules* **1998**, *31*, 314.
21. Goiti, E.; Huglin, M. B.; Rego, J. M. *Polymer (Guildf)* **2001**, *42*, 10187.
22. Gheneim, R.; Perez-Berumen, C.; Gandini, A. *Macromolecules* **2002**, *35*, 7246.
23. Tian, Q.; Yuan, Y. C.; Rong, M. Z.; Zhang, M. Q. *J. Mater. Chem.* **2009**, *19*, 1289.
24. Zhang, Y.; Broekhuis, A. A.; Picchioni, F. *Macromolecules* **2009**, *42*, 1906.
25. Toncelli, C.; De Reus, D. C.; Picchioni, F.; Broekhuis, A. A. *Macromol. Chem. Phys.* **2012**, *213*, 157.
26. Yoshie, N.; Saito, S.; Oya, N. *Polymer (Guildf)* **2011**, *52*, 6074.
27. Kennedy, J. P.; Castner, K. F. *J. Polym. Sci. Polym. Chem. Ed.* **1979**, *17*, 2055.
28. Chen, X.; Ruckenstein, E. *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 4390.
29. Lv, W.; El-Hebshi, Y.; Li, B.; Xia, Y.; Xu, R.; Chen, X. *Polym. Test.* **2013**, *32*, 353.
30. Murphy, E. B.; Bolanos, E.; Schaffner-Hamann, C.; Wudl, F.; Nutt, S. R.; Auad, M. L. *Macromolecules* **2008**, *41*, 5203.
31. Stille, J. K.; Plummer, L. *J. Org. Chem.* **1961**, *26*, 4026.
32. Drent, E.; Keijsper, J. J. (Shell Oil Co.). U.S. Pat. 5,225,523, July 6, **1993**.
33. Toncelli, C.; Reus, D. De; Broekhuis, A. A.; Picchioni, F. In *Self-Healing at the Nanoscale*; Taylor & Francis Group, Ed.; CRC Press: London, United Kingdom, **2011**; pp 199–248.
34. Clare, B. *Theor. Chim. Acta* **1994**, *87*, 415.
35. Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 4388.
36. Zhang, Y.; Broekhuis, A. A.; Stuart, C. A. M.; Picchioni, F. *J. Appl. Polym. Sci.* **2008**, *107*, 262.
37. Krimm, S. *Pure Appl. Chem.* **1968**, *16*, 369.
38. Josien, M.; Fuson, N. *J. Chem. Phys.* **1954**, *22*, 1169.
39. Peng, Y. X.; Liu, J. L.; Cun, L. F. *J. Polym. Sci. Part A: Polym. Chem.* **1996**, *34*, 3527.
40. Long, J.; Wang, X.; Zhang, G.; Dong, J.; Yan, T.; Li, Z.; Fu, X. *Chem. Eur. J.* **2007**, *13*, 7890.
41. Jong Se, P.; Takahashi, K.; Guo, Z.; Wang, Y.; Bolanos, E.; Hamann-Schaffner, C.; Murphy, E.; Wudl, F.; Hahn, H. T. *J. Compos. Mater.* **2008**, *42*, 2869.
42. Park, J. S.; Kim, H. S.; Thomas Hahn, H. *Compos. Sci. Technol.* **2009**, *69*, 1082.
43. Duenas, T.; Bolanos, E.; Murphy, E.; Mal, A.; Wudl, F.; Schaffner, C.; Wang, Y.; Hahn, H. T.; Ooi, T. K.; Jha, A.; Bortolin, R.; Aeronautics, N.; Angles, L.; Angeles, L.; Arsenal, R. *Multifunctional Self-Healing and Morphing Composites*, **2005**.
44. Blinco, J. P.; Trouillet, V.; Bruns, M.; Gerstel, P.; Gliemann, H.; Barner-Kowollik, C. *Adv. Mater.* **2011**, *23*, 4435.
45. Murphy, E. B. *J. Mater. Chem.* **2011**, *21*, 1438.
46. Teramoto, N.; Niwa, M.; Shibata, M. *Materials (Basel)* **2010**, *3*, 369.