

# Polyolefin thermoplastic elastomers from 1-octene copolymerization with 1-decene and cyclopentene

Ivana Pierro,<sup>a,b</sup> Giuseppe Leone,<sup>a,\*</sup> Giorgia Zanchin,<sup>a,c</sup>

Maurizio Canetti,<sup>a</sup> Giovanni Ricci,<sup>a</sup> Fabio Bertini<sup>a,\*</sup>

<sup>a</sup> Istituto per lo Studio delle Macromolecole – CNR, via A. Corti 12, 20133-Milano (Italy).

<sup>b</sup> Dipartimento di Scienze Chimiche, Università degli Studi di Napoli “Federico II”, via Cintia, 80126-Napoli (Italy).

<sup>c</sup> Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133-Milano (Italy).

\* Corresponding author.

*E-mail addresses:* giuseppe.leone@ismac.cnr.it (G. Leone) fabio.bertini@ismac.cnr.it (F. Bertini)

## Abstract

Thermoplastic elastomers (TPEs) are attractive materials because they combine the processing advantages and recycling potential of thermoplastics with the flexibility, low modulus, and soft touch of elastomers. In this article, the synthesis, characterization and mechanical properties of polyolefin TPEs are reported. A facile procedure is employed, through the chain-walking polymerization, to fabricate random copolymers of 1-octene with 1-decene and cyclopentene. The effect of the type and the feedstock comonomers concentration on the microstructure, the total branching and the branch-type distribution is studied. A comprehensive investigation on the mechanical behavior by uniaxial stretching until failure, step-cycle and creep tensile tests is carried out. All the copolymers behave as elastomers, with different mechanical properties strongly depending on the composition, structure and crystallinity.

**Keywords:** Thermoplastic elastomers, Polyolefins, 1-Octene copolymers, Cyclopentene, Mechanical properties, Nickel.

## 1. Introduction

For many years the key building blocks in the poly(olefin)s industry have been ethylene and propylene mainly due to their availability and low cost. Although these monomers are still useful today, the improved availability of C6–C20  $\alpha$ -olefins and cyclic olefins (*i.e.*, cyclopentene, norbornene and dicyclopentadiene) allows the fabrication of a wide array of homo- and copolymers alternative to poly(ethylene) (PE) and poly(propylene). For instance, copolymerization of ethylene with 1-octene gives LLDPE which has superior properties as packaging materials [1,2], while copolymers of ethylene with cyclic olefins are used in coatings for high-capacity CDs and DVDs, optical lenses, medical equipments, blisters, and toner binder [3,4]. In addition, thermoplastic elastomers (TPEs) fabricated from  $\alpha$ -olefins and ethylene [5-7], are a valued alternative to styrene and dienes materials not only in terms of properties but also due to the biorenewability of the monomers. Indeed, ethylene can be sourced by dehydration of bioethanol [8], and  $\alpha$ -olefins through ethylene oligomerization [9] and ethenolysis of fatty acids [10].

TPEs are easier and greener to process than thermosets and are used in many applications like automotive interiors, adhesives, electronics, flexible packaging films, sporting goods, and medical devices. TPEs combine the processing advantages and recycling potential of thermoplastics with the flexibility, low modulus, and soft touch of elastomers [11,12]. A two-phase molecular structure gives TPEs their combination of strength and flexibility: amorphous domains in the polymer are soft and provide its elastomeric nature, while the hard crystalline segments, usually dispersed throughout the amorphous matrix, form physical cross-links that give tensile strength, resistance to chemicals and heat and produce recoverable elasticity after strain-induced deformation [13]. Crucial in TPEs is the distribution of the crystalline domains, the properties of these materials

being strongly associated with the reorganization and deformation of the hard and amorphous regions [14-18].

There are various approaches for fabricating polyolefin TPEs [19-23] which have been recently summarized by Coates et al. [24]. Research in this field has mainly focused on the development of  $\alpha$ -diimine Pd(II) and Ni(II) complexes [25-36]. The peculiarity of these complexes is the ability of the active site to “walk” on the growing polymer chain during the propagation step (chain-walking) so that the new incoming monomer is assembled onto the polymer backbone rather than at the end, thus giving branched polymers [37]. Moreover, when the polymerization involves  $\alpha$ -olefins with a high number of carbon atoms a different enchainment becomes competitive: a significant fraction of monomer insertions occur in a 2,1 manner followed by chain-walking to the terminal  $\omega$  carbon atom of the growing polymer chain before successive monomer insertion (chain-straightening) [38-40]. The result of this  $\omega$ ,1-enchainment is the placement of linear semicrystalline PE-like segments (Scheme 1). By exploiting this mechanism, block copolymers with segments from linear (semicrystalline) to highly branched (amorphous) can be obtained by changing the monomer pressure, monomers feedstock concentration [41], and polymerization temperature [42], all parameters that regulate the competition between chain-walking and chain-propagation. In addition, the development of regioselective late transition metal complexes is an elegant approach to tune the competition between the chain-walking and chain-propagation, thus fabricating polymers with competitive thermal and tensile properties [43-45]. As an example, Coates and coworkers, using a living, regioselective aryl-naphthyl- $\alpha$ -diimine Ni(II) complex, synthesized multiblock TPEs from 1-decene and ethylene with strain at break up to 750% and elastic recovery up to 85% [24].

In this context, our group reported the synthesis and mechanical properties of different polyolefin TPEs with the use of a Ni(II)  $\alpha$ -diimine complex (i.e., Ni-1, Scheme 1). We synthesized di- and tri-block copolymers from 1-dodecene and ethylene with high strain values (about 1000%) but high permanent deformations after stretching (35% recovery after 10 cycles of 300% strain)

[41], and 1-octene polymers with strain break values up to 1300% and improved elastic strain recoveries [46]. We found that the type of the aluminum alkyl cocatalyst, the monomer feedstock concentration and the polymerization temperature were effective parameters which can be changed to tune the polymers microstructure and crystallinity which in turn strongly affects the thermal and mechanical properties.

The present work extends our previous studies with the aim to find alternatives to finely modulate the structure and properties of polymers from of 1-octene, allowing access to TPEs with valuable mechanical properties from readily accessible and potential biorenewable starting materials. A series of 1-octene copolymers with 1-decene and cyclopentene is synthesized, and a comprehensive investigation on the mechanical behavior by uniaxial stretching until failure, step-cycle and creep tensile tests is carried out.

## **2. Experimental**

### *2.1. Materials*

Manipulations of air- and/or moisture-sensitive materials were carried out under an inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk-line techniques. Toluene (Aldrich, > 99.5% pure) was refluxed over Na for 8 h and then distilled and stored over molecular sieves under nitrogen. Et<sub>2</sub>AlCl (Aldrich) was used as received. Ni-1 (Scheme 1) was synthesized according to the literature [47]. 1-Octene (Aldrich, 98% pure), 1-decene (Aldrich, 95% pure) and cyclopentene (Aldrich, 96% pure) were refluxed over CaH<sub>2</sub> for 4 h, then distilled via trap-to-trap and, finally, stored under nitrogen and kept at -15 °C. Deuterated solvent for NMR measurements (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>) (Cambridge Isotope Laboratories, Inc.) was used as received.

### *2.2. Polymerization*

Polymerizations were carried out in a 25 mL Schlenk flask. The reactor was first dried by heating at 110 °C and then vacuum was applied for 1 h. Toluene, (co)monomers, Et<sub>2</sub>AlCl and a toluene solution of Ni-1 (2 mg/mL) were transferred into the reactor vessel in that order.

Polymerization was quenched with methanol containing a small amount of hydrochloric acid. The precipitated polymers were collected by filtration, repeatedly washed with fresh methanol and then dried to constant weight.

### 2.3. Characterization

For  $^{13}\text{C}$  NMR, about 80 mg of the polymer was dissolved in  $\text{C}_2\text{D}_2\text{Cl}_4$  in a 10 mm tube. HDMS (hexamethyldisiloxane) was used as internal chemical shift reference. The spectra were recorded on a Bruker NMR AVANCE 400 Spectrometer operating at 100.58 MHz ( $^{13}\text{C}$ ) in the PFT mode working at 103 °C. The applied conditions were the following: 10 mm probe, 90° pulse angle; 64 K data points; acquisition time 5.56 s; relaxation delay 20 s; 3–4K transient. Proton broad-band decoupling was achieved with a 1D sequence using *bi\_waltz\_16\_32* power-gated decoupling.  $^1\text{H}$  NMR spectroscopy was used to determine overall branching [48].  $^{13}\text{C}$  NMR spectroscopy was used to examine the types of branches. The quantitative analysis was based on the equations reported by Galland et al. [42].

The molecular weight average ( $M_n$ ) and the molecular weight distribution ( $M_w/M_n$ )—were obtained by a high temperature Waters GPCV2000 size exclusion chromatography (SEC) system using a refractometer detector. The experimental conditions consisted of three PL Gel Olexis columns, *o*-DCB as the mobile phase, 0.8 mL/min flow rate, and 145 °C. The calibration of the SEC system was constructed using eighteen narrow  $M_w/M_n$  polystyrene standards with molar weights ranging from 162 to  $5.6 \times 10^6$  g/mol. For SEC analysis, about 12 mg of polymer was dissolved in 5 mL of *o*-DCB with 0.05% of BHT as antioxidant.

Differential scanning calorimetry (DSC) measurements were performed on a Perkin–Elmer DSC 8000 instrument equipped with a liquid nitrogen device. The scans were carried out from –100 to 125 °C under nitrogen atmosphere using heating and cooling rates of 10 °C/min.

Wide angle X-ray diffraction (WAXD) data were obtained at 18 °C using a Siemens D-500 diffractometer equipped with a Siemens FK 60-10 2000W tube (Cu  $K_\alpha$  radiation,  $\lambda = 0.154$  nm).

The operating voltage and current were 40 kV and 40 mA, respectively. The data were collected from 5 to 35  $2\theta$  0.02  $2\theta$  intervals.

Small angle X-ray scattering (SAXS) measurements were conducted at 18 °C with a Kratky Compact Camera. Monochromatized Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) was supplied by a stabilized Siemens Krystalloflex 710 generator and a Siemens FK 60-10 2200 W Cu target tube operated at 40 kV and 45 mA. The scattered intensity was counted in different angular ranges by using a step scanning proportional counter with pulse height discrimination, the abscissa variable was  $h = \sin(\theta) 4\pi/\lambda$ , the data were successively corrected for blank scattering and desmeared. The internal surface of the polymers was calculated as proposed by the Porod approach for non-particulate system [49].

The materials for the mechanical characterization were molded in a heated press at 90 °C and 50 bar for 5 minutes, then the press plates were cooled at 20 °C/min to room temperature. Films with a thickness of 120–150  $\mu\text{m}$  were produced. Tensile dog-bone-shaped specimens (length overall 75 mm, gauge length 25 mm, and width of narrow section 4 mm) were analyzed at 19 °C using a Zwick Roell ProLine Z010 mechanical tester equipped with a XforceP (50 N) load cell at a constant crosshead rate of 15 mm/min. In the hysteresis experiments performed at various strains, the specimens were cyclically loaded and unloaded in uniaxial tension. In the creep experiment the specimens were elongated to 300% strain and held at a constant stress for 3 h.

### 3. Results and Discussion

Ni-1/Et $_2$ AlCl was selected for the copolymerization of 1-octene (OCT) with 1-decene (DE) and cyclopentene (CPE) because it has been investigated in detail in the polymerization of higher linear  $\alpha$ -olefins, which allows a good comparison [41,46]. 1-Decene and cyclopentene were chosen because it was expected that their incorporation in the polymer chain may lead to more linear microstructure [24,50,51]. Moreover, cyclopentene has been largely investigated in the olefin

copolymerization to give copolymers of outstanding thermal, optical and mechanical properties [51-56].

### 3.1. Copolymerization of 1-octene with 1-decene

A series of experiments was carried out at different comonomers feedstock compositions (OCT/DE from 4.0 to 0.25) while the total concentration was kept at 1.0 mol/L, this concentration being optimal to obtain high yield and polymers with valuable mechanical properties [41,46]. The results are summarized in Table 1.

Ni-1/Et<sub>2</sub>AlCl shows good activities for the polymerization of 1-octene and 1-decene, the former being consumed slightly faster (Table 1, entry 1 vs 2) to give branched PE-like materials with high molecular weight and narrow molecular weight distribution. The exclusive 1,2-enchainment would result in a poly(1-octene) with 125 branches/1000C, and a poly(1-decene) with 100 branches/1000C. However, the effective branching level of the resulting homopolymers is almost half of the theoretic value (*i.e.*, 66 and 55/1000C for 1-octene and 1-decene polymers, respectively) which is the result of the fact that the nickel center can uniquely walk along the growing polymer chain, rendering branches of various lengths [57]. This result confirms that Ni-1 is poorly regioselective: it do not have a significant selectivity for 2,1- and 1,2-insertion regardless of the length of the monomer [41].

Good activities were also obtained for the copolymerization of 1-octene with 1-decene with product obtained in the order of grams. The resulting copolymers have high molecular weight, narrow molecular weight distribution from 1.43 to 1.51, and branches/1000C of 69 at OCT/DE = 4, 63 at OCT/DE = 1 and 62 at OCT/DE = 0.25 (Table 1, entries 3–5).

The polymers were analyzed by <sup>13</sup>C NMR (Fig. 1). Total methyls and branching distribution are quantitatively calculated on the basis of previous resonance assignments [42], and reported in Table 2. The nomenclature used for isolated branches is that of Usami and Takayama [58]. Sample 3, obtained at OCT/DE = 4, exhibits the highest content of branching. The basic trend is that the total methyls of the resulting copolymers decrease with increasing the 1-decene feedstock

concentration, thus confirming that the density of branches is primarily controlled by the monomer length [41]. All the polymers have predominantly methyl and longer than butyl branches (Me and Lg in Table 2, respectively): the intense signal at 27.73 ppm of long  $-\text{CH}_2-$  sequences and signals due to methyl (1B1 at 17.86 ppm is **1'** in Fig.1) and longer branches (1Bn at 12.01 ppm and 2Bn at 20.68 ppm are **1** and **2** in Fig.1, respectively) are safely identified in the  $^{13}\text{C}$  NMR spectra (Fig. 1A). Carbons of ethyl and butyl branch (1B2 and 2B4 at 9.0 and 21.1 ppm, respectively) are absent, while a very weak signals due to a propyl branch (1B3 at 12.86 ppm) is observed. Moving 1-octene concentration from 0.8 to 0.2 mol/L, the content of methyls decreases from 31 to 23/1000C and, likewise, the content of longer branches drops from 33 to 30/1000C (Table 2, entries 3–5). It is worth mentioning that the predominance of longer branches means that successive 1,2-insertions (1,2-enchainment) are faster than a 1,2-insertion followed by chain-walking ( $\omega$ ,2-enchainment) [43].

DSC of OCT/DE copolymers revealed a thermal behavior similar to those displayed by poly(olefin)s made by Ni-1/Et<sub>2</sub>AlCl [41,46]. The cooling DSC trace shows a relative sharp crystallization exotherm followed by a wide tail (Fig. 2A). The crystallization temperature ( $T_c$ ) taken at the maximum of the sharp peak increases progressively with the increasing of 1-decene feedstock concentration (Table 2). The heating curves of the non-isothermal crystallized OCT/DE copolymers exhibit a glass transition event at low temperature, ranging from  $-48$  to  $-45$  °C, and a broad melting endotherm (Fig. 2B). In general, as the 1-decene feedstock concentration increased the melting point and the melting enthalpy of the obtained copolymer increase ( $T_m$  and  $\Delta H_m$  in Table 2, respectively). These data are strictly related to the copolymers microstructure. Indeed, a decrease in the content of branches longer than methyl produce a corresponding increase in crystallization temperature ( $T_c$ ),  $T_m$ , and  $\Delta H_m$  of the copolymer (Table 2). In this regard, it is worth noting that poly(1-decene) and the copolymer obtained at low OCT/DE ratio, which have similar total branching and longer side groups content, exhibit very similar  $T_c$ ,  $T_m$  and crystallinity (Table 2, entry 2 and 5, respectively)



### 3.2. Copolymerization of 1-octene with cyclopentene

Copolymerizations of 1-octene with cyclopentene were performed at three different OCT/CPE ratio from 1.4 to 0.5, keeping constant the 1-octene feedstock concentration of 1.0 mol/L. The results are summarized in Table 3. Under the employed conditions, Ni-1/Et<sub>2</sub>AlCl exhibits no activity toward the cyclopentene homopolymerization. The productivities of OCT/CPE copolymerizations are modest, but markedly increase with increasing the polymerization time (Table 3, entry 6 vs 8). Indeed, the presence of cyclopentene in the polymerization mixture slows the polymerization rate, and hence the catalytic activity (entry 7 in Table 3 vs entry 2 in Table 1), as found by Ye et al. [51] and Zhu et al. [59] for the copolymerization of ethylene with CPE. All the copolymers, obtained at longer polymerization time (Table 3, entries 7–9), have molecular weights greater than  $150 \times 10^3$ , narrow molecular weight distribution (from 1.36 to 1.62), excellent solubility in common organic solvents at room temperature, and low cyclopentene incorporation. The CPE content in the copolymers increases from 4.2 to 6.5 mol% increasing the comonomer feedstock concentration from 0.7 to 2.1 mol/L (Table 3, entries 7–9).

The copolymers were studied by <sup>13</sup>C NMR. According to the assignments by Müller [60], the predominant copolymers microstructure is sketched in Fig. 1B. The OCT/CPE copolymers have all the NMR peaks exhibited by the <sup>13</sup>C NMR of the homopolymer, meaning the presence of branched structures in the copolymers. In addition, some new peaks are also found in the spectra of the copolymers, whose intensity increases by increasing the CPE incorporation. These peaks can be attributed to the carbon atoms of the five-membered CPE isolated unit in the *cis*-1,3-enchained form, namely at 38.84 (C2), 38.38 (C1, C3) and 29.92 ppm (C4, C5) [51, 59], and carbons of ethylene units in the vicinity of the rings, *i.e.*,  $\alpha''$ ,  $\beta''$ ,  $\gamma''$  at 34.7, 26.9 and 27.9 ppm, respectively (Fig. 1B) [61]. In contrast, no resonances are observed in regions that would clearly identify 1,2-enchained CPE units: the 1,3-enchainment of CPE is attributed to the rapid isomerization of the last 1,2-inserted CPE unit by a  $\beta$ -H elimination–reinsertion process (Scheme 2) [62,63]. In addition, a peak at about 15.6 ppm (marked as Y in Fig. 1B), whose intensity slightly increases with increasing

the CPE content in the copolymers, was registered in the  $^{13}\text{C}$  NMR spectra of OCT/CPE copolymers. Peak Y should be assigned to the  $\text{CH}_3$  carbon of a new branching structure in the vicinity of the last-inserted CPE unit. By comparison with the chemical shift of propylene/CPE copolymers [64], peak Y has been assigned to a methyl branch close to the repeating ring unit formed through the 1,2-insertion of 1-octene on the last-inserted CPE followed by chain-walking (8,2-enchainment in Scheme 3).

The obtained copolymers are moderately branched with a total branching which drops from 72 to 62/1000C with increasing the CPE content in the copolymers. Table 4 lists the branch distribution of the copolymers. Generally, the copolymers exhibit two major branch lengths, namely methyl and longer than butyl branches (Me and Lg in Table 4, respectively). By increasing the CPE incorporation, methyl branches decrease from 33 to 25/1000C and longer branches from 38 to 36/1000C. Currently, a conclusive mechanistic rationale is not possible. A plausible explanation of the fact that methyl branches decrease much more than longer branches is that when CPE is the last-inserted unit, the formation of a methyl adjacent to the ring (8,2-enchainment in Scheme 3) may be disfavored with respect to the formation of a longer branch close to the CPE (1,2-enchainment in Scheme 3). This is because to give a methyl branch close to the CPE, the nickel center has to walk through a CH carbon, which could disallow the nickel from walking through [65].

The thermal behavior of OCT/CPE copolymers was investigated by DSC and the thermograms are reported in Fig. 3. The DSC curves of the copolymers show similar features as found for poly(1-octene) prepared at the same 1-octene feedstock concentration (1.0 mol/L). In particular, all the copolymers exhibit a sharp crystallization peak in the cooling scan (Fig. 3A) and a broad endothermic transition beginning at subambient temperatures in the heating scan (Fig. 3B). Nevertheless, OCT/CPE copolymers exhibit reduced  $T_c$ ,  $T_m$  and melting enthalpy with respect to poly(1-octene) (entry 1 in Table 2). Increasing the CPE incorporation in the copolymers,  $T_c$  and  $T_m$  shift to lower temperatures and the  $\Delta H_m$  value decreases, which is the result of the reduced crystallinity due to the CPE ring incorporation. The presence of rigid CPE moiety ensures higher

$T_g$ s than that obtained for reference poly(1-octene) ( $T_g = -49$  °C, entry 1 in Table 2), and the  $T_g$  value slightly increases with increasing the CPE content.

### 3.3. Structure and Mechanical Properties

The synthesized copolymers were structurally characterized by X-ray techniques. WAXD patterns show a diffuse peak centred at about  $20$   $2\theta^\circ$ , while the typical diffractions of the poly(ethylene) orthorhombic crystalline phase were not evidenced (Fig. 4A). Therefore, the low melting temperature and broad melting range of the copolymers can be likely due to the fringed-micellar crystal structure with a broad size distribution that comes from the statistical distribution of crystallizable chain lengths. In this respect, Bensason et al. [66] and Peeters et al. [67] showed that the crystallinity of ethylene/1-octene copolymers is influenced by the comonomer content and the decrease in the crystallinity degree determines a gradual change from a completely lamellar morphology to a granular crystals morphology, where the crystalline regions are described as fringed micelles.

The supermolecular structure of 1-octene copolymers was investigated by SAXS. In Fig. 4B, the Lorentz corrected plots of sample 3 and 8 are shown. SAXS profile displays the presence of a maximum, which is associated to the periodicity that results from the electron density difference between crystalline and amorphous phases. The long periods ( $L_p$  in Table 5) deduced from the Lorentz plots result almost constant for OCT/DE copolymers (about 11 nm), while OCT/CPE copolymers show higher  $L_p$  value ranging from 11.8 to 13.4 nm with increasing the CPE content in the copolymers (Table 5). SAXS data were elaborated to calculate the internal surface ( $O_s$ ) considering that the crystallinity of the polymers is due to the presence of fringed micellar crystals, consisted of bundles of parallel chain segments randomly dispersed in an amorphous matrix. The  $O_s$  values calculated for OCT/CPE copolymers resulted markedly lower than those of OCT/DE copolymers (Table 5). These results suggest a different morphology between the copolymer series in terms of dimension of fringed-micellar crystals and their dispersion in the amorphous matrix.

First investigation on the mechanical behavior of the copolymers was performed at 19 °C by uniaxial stretching until failure. Representative stress-strain curves are depicted in Fig. 5 and the tensile properties are reported in Table 5. All samples show stress-strain curves with typical features of elastomers, *i.e.*, low modulus, uniform deformation to high strain and strain hardening at the late stage of deformation. Comparing the tensile behaviour of OCT/DE copolymers and reference homopolymers (entry 1 and 2), one can notice some differences (Fig. 5A). The initial modulus depends only on the crystallinity of the polymer ranging from 5.4 to 7.5 MPa with increasing the crystallinity. A stress upswing, characterized by an increasing slope in the stress-strain curve, is observed for all the materials and the onset of strain hardening occurs at different strain as a function of the copolymer composition. Sample 5, prepared at higher feedstock concentration of 1-decene, and poly(1-decene) (entry 2) exhibit stronger strain hardening with ultimate tensile strength of about 16 MPa. The OCT/DE copolymers and the homopolymers show high and comparable ultimate strain around 1350%. Taking into account that the investigated polymers have similar molecular weight and narrow molecular weight distribution, the differences in stress-strain behavior are attributed to differences in microstructure and composition. Indeed, the copolymer obtained at OCT/DE = 4 (entry 3) exhibits tensile properties close to those of poly(1-octene) (entry 1), whereas the copolymer obtained at OCT/DE = 0.25 (entry 5) shows a tensile behavior very similar to that of poly(1-decene) (entry 2). Moreover, the stress-strain behavior of sample 4 (OCT/DE = 1) is intermediate between that of sample 3 and 5.

The stress-strain curves of OCT/CPE copolymers and reference poly(1-octene) (entry 1) are shown in Fig. 5B. Compared to sample 1, the copolymers have lower Young's modulus between 3.2 and 3.8 MPa and lower ultimate tensile strength in the range from 8.0 to 9.4 MPa. The lower modulus and tensile strength of the copolymers are related to the reduced crystallinity due to the CPE incorporation in the polymer backbone. As regards the elongation at break, the copolymers present high strain fractures similar to that of reference homopolymer. The elongation at break value slightly increases with increasing the CPE content (Table 5).

All the investigated materials were also subjected to step cycle tensile tests to determine the elastic recovery. In the first set of experiments, the samples were cyclically loaded and unloaded ten times to 300% strain, based on the initial gauge length. All the samples exhibit a certain amount of unrecovered strain after the 1st cycle with only a small increase in the unrecovered strain on each subsequent cycle (Fig. 6A). Therefore, a permanent structural change takes place during the first conditioning cycle, and a material with better elastomeric properties is created. From the stress-strain curve the strain recovery (SR) can be calculated as  $SR = 100 (\varepsilon_a - \varepsilon_r) / \varepsilon_a$ , where  $\varepsilon_a$  is the applied strain and  $\varepsilon_r$  is the strain in the cycle at zero load after the applied strain. For OCT/DE copolymers, the recovery strain after the first load cycle ranges from 58 to 64% and increases with decreasing the polymer crystallinity ( $SR_I$  in Table 5). The OCT/DE copolymers show a slight decreasing trend in the strain recovery with the load cycle times, whereas the order of the strain recovery remains unchanged (Fig. 6B). The OCT/CPE copolymers display similar recovery over the whole cycle tensile test and the highest elastic recovery of about 57% after the last load cycle ( $SR_X$  in Table 5).

In the second set of cyclic experiments, the samples were extended step by step up to different strains. As a typical example, the stress-strain curve during cyclic tensile deformation of sample 9 is shown in Fig. 7A. The strain recovery decreases rapidly at lower applied strains and then levels off at higher applied strains (Fig. 7B). For OCT/DE copolymers, the elastic recovery over the whole range of deformations decreases with increasing the copolymers crystallinity. In particular, sample 3, obtained from the highest feedstock concentration of 1-octene, exhibits strain recoveries close to that of poly(1-octene), whereas sample 5 from the lowest feedstock concentration of 1-octene, shows a behavior very similar to that of poly(1-decene). All the OCT/CPE copolymers exhibit strain recovery higher than the reference poly(1-octene), sample 7, with a CPE content of 4.2 mol%, presenting the highest elastic recovery (about 66%) for the whole range of applied strains.

Copolymers were subjected to creep experiments in order to evaluate their resistance to permanent deformation. Samples were elongated to 300% strain and held at a constant stress for 3 h. It is worth pointing out that every sample required typical stress value in order to achieve 300% strain (from 1.5 to 2.8 MPa). Selected strain-time curves are shown in Fig. 8A. The OCT/CPE copolymers exhibit the higher deformation over time, particularly sample 9 with the highest CPE content and the lowest crystallinity. The OCT/DE copolymers show improved resistance to strain-induced deformation compared to OCT/CPE copolymers, sample 5, obtained from copolymerization with the highest feedstock concentration of 1-decene, exhibiting the least amount of deformation. The creep behavior of reference poly(1-octene) is intermediate between that of the two copolymer series.

Altogether, the tensile tests show that the investigated copolymers behave as elastomers with properties close to those reported for TPEs of random ethylene/ $\alpha$ -olefin copolymers [24, 68-71]. Moreover, it is worth emphasizing that these materials retain excellent mechanical properties, *i.e.* high elongation at break and ultimate tensile strength, and good strain recovery, even after being melted and reprocessed several times (Fig. 8B).

#### 4. Conclusions

A chain-walking copolymerization approach for the synthesis of TPEs from readily accessible and inexpensive starting materials is reported. Three sets of OCT/DE and OCT/CPE random copolymers are synthesized with the use of an  $\alpha$ -diimine Ni(II) complex. The resulting copolymers are composed of long methylene segments, methyl branches formed by 1,2-monomer insertion followed by chain-walking ( $\omega$ ,2-enchainment), and longer branches by successive 1,2-insertions (1,2-enchainment). In the case of OCT/CPE copolymers, the ring content (in the range from 0.8 to 6.5 mol%) was effectively tuned by changing the feedstock comonomer concentration. CPE is mainly incorporated in the copolymers in the form of isolated *cis*-1,3 units. The thermal properties and crystallinity of the resulting copolymers are strongly determined by their microstructure: the presence of long branches and rigid ring units interferes on the crystallization

and melting behaviour. The low melting temperature and broad melting range of the copolymers are attributed to the fringed-micellar crystal structure with a broad size distribution.

The tensile tests show that the 1-octene copolymers behave as TPEs exhibiting a low modulus, a uniform deformation to high strain and an instantaneous strain recovery. The Young's modulus and tensile strength of the copolymers increases with crystallinity, while the ultimate strain result quite constant. The hysteresis and creep tests show that the elastic recovery and deformation in strain over time are mainly influenced by the copolymers crystallinity. The OCT/CPE copolymers are found to have better strain recovery than homopolymers and OCT/DE copolymers, while the latter are more resistant to deformation.

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**Table 1.** Polymerization of 1-octene (OCT), 1-decene (DE) and copolymerization of OCT with DE catalyzed by Ni-1/Et<sub>2</sub>AlCl<sup>a</sup>.

Entry	OCT (mol/L)	DE (mol/L)	OCT/DE (mol/mol)	$M^b$ (mol/L)	Yield		$M_n^c$ ( $\times 10^{-3}$ )	$M_w/M_n^c$	Branches/1000C <sup>d</sup>
					(g)	(%)			
1 <sup>e</sup>	1.0			1.0	1.1	58	105.6	1.36	66
2		1.0		1.0	0.9	43	115.3	1.42	55
3	0.8	0.2	4.0	1.0	1.1	58	117.5	1.51	69
4	0.5	0.5	1.0	1.0	1.2	61	126.4	1.43	63
5	0.2	0.8	0.25	1.0	1.3	62	126.8	1.46	62

<sup>a</sup> Polymerization conditions: toluene, total volume, 16 mL; Ni-1, 10  $\mu$ mol; Al/Ni molar ratio, 200; temperature, 22 °C; time, 3 h.

<sup>b</sup>  $M$  is the total (co)monomers feedstock concentration.

<sup>c</sup> Molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) from SEC.

<sup>d</sup> From <sup>1</sup>H NMR.

<sup>e</sup> Data reported in Ref. [41].

**Table 2.** Microstructural data and thermal properties for OCT/DE copolymers.

Entry	CH <sub>3</sub> /1000C <sup>a</sup>		total CH <sub>3</sub> <sup>a</sup>	$T_g^b$ (°C)	$T_c^b$ (°C)	$T_m^b$ (°C)	$\Delta H_m^b$ (J/g)	$X_{DSC}^c$ (%)
	Me	Lg						
1	27	32	60	-49	32	49	29	10.0
2	21	30	51	-45	35	55	34	11.7
3	31	33	65	-48	32	49	30	10.3
4	23	31	55	-46	33	53	33	11.4
5	23	30	54	-45	35	56	34	11.7

<sup>a</sup> From <sup>13</sup>C NMR. A small amount (never exceeding 1 CH<sub>3</sub>/1000C) of propyl branches was observed.

<sup>b</sup> From DSC.

<sup>c</sup> Crystallinity from melting enthalpy,  $X_{DSC} = (\Delta H_m / \Delta H_m^0) \times 100$ ,  $\Delta H_m^0 = 290$  J/g.



**Table 3.** Copolymerization of OCT with CPE catalyzed by Ni-1/Et<sub>2</sub>AlCl<sup>a</sup>.

Entry	OCT (mol/L)	CPE (mol/L)	OCT/CPE (mol/mol)	$M^b$ (mol/L)	time (h)	Yield		CPE <sup>c</sup> (mol%)	$M_n^d$ ( $\times 10^{-3}$ )	$M_w/M_n^d$
						(g)	(%)			
6	1.0	1.4	0.7	2.4	3	0.40	12	0.8	78.4	1.29
7	1.0	0.7	1.4	1.7	22	1.75	69	4.2	159.0	1.62
8	1.0	1.4	0.7	2.4	22	1.50	45	5.6	174.7	1.41
9	1.0	2.1	0.5	3.1	22	1.50	37	6.5	165.8	1.36

<sup>a</sup> Polymerization conditions: toluene, total volume, 16 mL; Ni-1, 10  $\mu$ mol; Al/Ni molar ratio, 200; temperature, 22  $^{\circ}$ C.

<sup>b</sup>  $M$  is the total (co)monomers feedstock concentration.

<sup>c</sup> From <sup>13</sup>C NMR.

<sup>d</sup> Molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) from SEC.

**Table 4.** Microstructural data and thermal properties for OCT/CPE copolymers.

Entry	CH <sub>3</sub> /1000C <sup>a</sup>		total CH <sub>3</sub> <sup>a</sup>	CPE <sup>a</sup> (mol%)	T <sub>g</sub> <sup>b</sup> (°C)	T <sub>c</sub> <sup>b</sup> (°C)	T <sub>m</sub> <sup>b</sup> (°C)	ΔH <sub>m</sub> <sup>b</sup> (J/g)	X <sub>DSC</sub> <sup>c</sup> (%)
	Me <sup>d</sup>	Lg <sup>e</sup>							
7	33	38	72	4.2	-45	25	43	23	7.9
8	26	36	63	5.6	-44	24	42	22	7.6
9	25	36	62	6.5	-43	22	39	20	6.9

<sup>a</sup> From <sup>13</sup>C NMR. A small amount of propyl branches (1 CH<sub>3</sub>/1000C) was observed.

<sup>b</sup> From DSC.

<sup>c</sup> Crystallinity from melting enthalpy, X<sub>DSC</sub> = (ΔH<sub>m</sub>/ΔH<sub>m</sub><sup>0</sup>)×100, ΔH<sub>m</sub><sup>0</sup> = 290 J/g.

<sup>d</sup> Me branches are calculated as the sum of isolated methyls as sketched in Figure 1B and methyl branches adjacent to the repeating unit from CPE (Scheme 3, 8,2-enchainement).

<sup>e</sup> Lg includes isolated longer branches as sketched in Figure 1B and longer branches close to the CPE ring (Scheme 3, 1,2- enchainement).

**Table 5.** Supermolecular parameters and mechanical properties.

Entry	$L_p^a$ (nm)	$O_s^a$ (m <sup>2</sup> /cm <sup>3</sup> )	$E^b$ (MPa)	$\sigma^b$ (MPa)	$\epsilon^b$ (%)	SR <sub>I</sub> <sup>c</sup>	SR <sub>X</sub> <sup>d</sup>	SR <sub>1200%</sub> <sup>e</sup>
1	11.2	89	5.4±0.2	10.2±1.0	1398±61	65	54	59
2	10.8	91	7.5±0.3	15.5±0.4	1388±29	59	47	53
3	10.8	93	5.7±0.4	12.5±0.4	1375±73	64	52	59
4	11.0	99	6.1±0.4	15.1±1.5	1291±33	61	49	56
5	11.0	98	7.3±0.2	16.0±1.3	1310±27	58	46	53
7	11.8	63	3.8±0.4	9.4±0.6	1260±85	69	57	66
8	12.1	64	3.7±0.2	9.1±0.2	1324±70	69	57	64
9	13.4	53	3.2±0.1	8.0±0.3	1424±41	69	56	61

<sup>a</sup> Long period ( $L_p$ ) and internal surface ( $O_s$ ) from SAXS.

<sup>b</sup> Young's modulus ( $E$ ), ultimate tensile strength ( $\sigma$ ) and elongation at break ( $\epsilon$ ).

<sup>c</sup> Strain recovery measured after the first step in a step cycle test type at 300% strain.

<sup>d</sup> Strain recovery measured after the last step in a step cycle test type at 300% strain.

<sup>e</sup> Strain recovery measured after the strain at 1200% in a step cycle test type at increasing strains.

## Captions

**Scheme 1.** Modes of enchainment for ethylene and  $\alpha$ -olefins by  $\alpha$ -diimine Ni(II) complexes.

**Scheme 2.** Isomerization mechanism for the generation of a 1,3-enchainment CPE unit.

**Scheme 3.** Modes of enchainment for 1-octene insertion on the last-inserted CPE unit.

**Fig. 1.**  $^{13}\text{C}$  NMR spectra and assignment of (A) OCT/DE copolymers ( $n = 4$  to  $6$ ), and (B) OCT/CPE copolymers ( $n = 4$ ).

**Fig. 2.** (A) DSC cooling scans of OCT/DE copolymers and reference homopolymers and (B) DSC successive heating scans.

**Fig. 3.** (A) DSC cooling scans of OCT/CPE copolymers and poly(1-octene) and (B) DSC successive heating scans.

**Fig. 4.** (A) WAXD profiles and (B) Lorentz corrected SAXS profiles of selected copolymers.

**Fig. 5.** Stress-strain curves of (A) OCT/DE copolymers and reference homopolymers and (B) OCT/CPE copolymers during monotonic tensile deformation.

**Fig. 6.** (A) Stress-strain curve of OCT/CPE copolymer (Table 3, entry 9) in the hysteresis experiments for a strain of 300% and (B) strain recovery as a function of cycle times.

**Fig. 7.** (A) Stress-strain curve of OCT/CPE copolymer (Table 3, entry 9) during step cycle tensile deformation at different strain and (B) strain recovery as a function of the applied strain.

**Fig. 8.** (A) Creep experiments of selected samples and (B) stress-strain curves of OCT/DE copolymer (Table 1, entry 5) during monotonic tensile deformation: comparison between pristine and reprocessed samples.