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# ROMP of novel hindered phenol-functionalized norbornenes and preliminary evaluation as stabilizing agents<sup>†</sup>

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## A B S T R A C T

A series of new norbornene monomers containing sterically hindered phenol groups have been synthesized and polymerized via ring-opening metathesis polymerization (ROMP) using the Grubbs 3<sup>rd</sup> generation catalyst (G3'). ROMPs exhibit first-order kinetics and molar masses increase linearly with monomer conversion and well-controlled phenol hindered-functionalized polynorbornenes were obtained with a monomer to initiator ratio up to 1 000. The first-order rate constants show that the ROMP activity is closely associated with the norbornene monomer steric congestion. The antioxidant behavior of these hindered phenol-containing polynorbornenes with different *para*-bridged side groups in polypropylene (PP) was estimated by onset oxidation temperature (OOT) measurements. The ability of these hindered phenol-containing norbornenes to copolymerize by ROMP with dicyclopentadiene (DCPD) was used to bound covalently the antioxidant moiety onto a polydicyclopentadiene (PDCPD) resin whose thermal ageing has been investigated.

### Keywords:

hindered phenol-containing norbornenes  
ring-opening metathesis polymerization (ROMP)  
kinetics  
stabilizing agents  
ageing

## 1. Introduction

Adding antioxidants has proved to be an effective method of slowing down the oxidation of polymers [1–3]. Among these species, hindered phenols have demonstrated their capacity to trap radicals and their effectiveness as stabilizers against the oxidation of polymers [4–7]. However, their effectiveness is limited over time by diffusion, evaporation or extraction phenomena which decrease their concentration in the stabilized material [8–10] and pose a potential environmental issue [11]. The two main approaches developed to retard the physical loss of antioxidants are (i) production of antioxidants with high molar mass [12,13] and (ii) chemically attach antioxidants to the polymer by copolymerization of an olefin with an antioxidant-functionalized vinyl [14,15] or norbornenyl [16–18] monomer or chemical modification of the polyolefin matrix [19–21]. For these purposes, hindered phenol-functionalized vinyl monomers have been (co)polymerized by the radical route [22], but generation of radicals during the polymerization process may induce reaction with antioxidant groups.

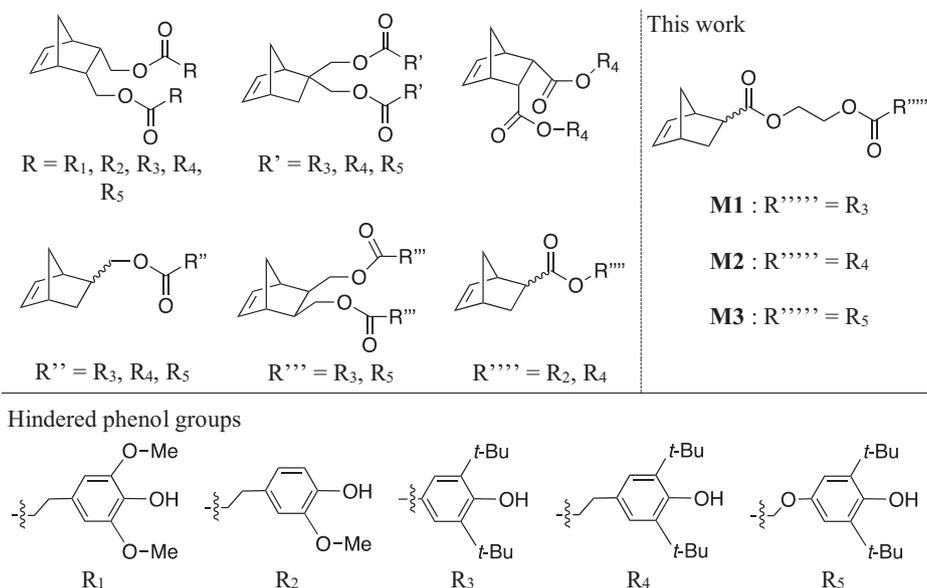
ROMP is an attractive method for preparing well-defined hindered phenol-functionalized polymers thanks to highly functional tolerant Grubbs initiators [23,24]. A number of norbornenes derivatives containing hindered phenol-containing norbornenes have successfully polymerized by ROMP to prepare the corresponding polymeric antioxidants (Scheme 1) [25–31].

Norbornenes bearing two sterically hindered phenols have been previously (co)polymerized using the first-generation Grubbs (G1) and second-generation Hoveyda-Grubbs (HG2) catalysts (R<sub>1</sub> and R<sub>2</sub>, Scheme 1) [27]. Polymers with number-average molar mass ( $\overline{M}_n$ ) of 7 000 g.mol<sup>-1</sup> and 22 000 g.mol<sup>-1</sup> and dispersities ( $\mathcal{D}$ ) ranging from 1.8 and 2.1 were obtained. The antioxidant activity of the resulting hydrogenated (co)polymers has been assessed by the 2,2-diphenyl-1-picrylhydrazyl (DPPH) test. Xue *et al.* have reported the synthesis and ROMP of a series of hindered phenol-containing norbornenes using G1 (R, R' = R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, Scheme 1) with high  $\overline{M}_n$  ranging from 19 900 et 1 022 500 g.mol<sup>-1</sup> and  $1.06 \leq \mathcal{D} \leq 2.78$  [28–30]. The antioxidant ability of the resulting polymers was determined by oxidation induction temperature (OIT) in polypropylene (PP).

2,6-Di-*tert*-butyl phenol norbornene has also been copolymerized with ethylene [16] or ethylene and norbornene [18] in the presence of a metallo-aluminoxane catalytic system. The resulting co- and terpolymers with tunable amounts of antioxidant

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**Scheme 1.** Structures of hindered phenol-containing norbornene monomers polymerized by ROMP reported in the literature and in this work.

functionalities dispersed in low-density polyethylenes and commercial grades of ethylene-norbornene copolymers have been shown to increase the thermo-oxidative resistance of the films by OIT measurements [17,18].

In the present work, novel 2,6-di-*tert*-butylphenol containing-norbornenes (**M1**, **M2** and **M3**, Scheme 1) have been synthesized from 2-hydroxyethyl-5-norbornene-2-carboxylate, resulting in monomers with different electronic donating effect of the substituent in *para*-position of antioxidant phenol group for an expected effect of the norbornene reactivity toward ROMP (R<sub>3</sub>, R<sub>4</sub> [29], R<sub>5</sub>, Scheme 1). Their ROMP has been investigated using the third-generation Grubbs catalyst [(H<sub>2</sub>IMes)(py)<sub>2</sub>(Cl)<sub>2</sub>Ru=CHPh] (G3'). The free radical trapping phenol efficiency of these antioxidant structures has been studied. Two approaches were applied to increase persistence of antioxidants in the polymeric matrix and avoid the physical loss of the low molar mass antioxidant commonly used for stabilizing commercial polyolefins due to diffusion and volatility [12–22]. Hindered phenol-functionalized polynorbornenes were then incorporated in PP and polydicyclopentadiene (PDCPD). The hindered phenol-functionalized norbornene **M1** has also been used as a comonomer of dicyclopentadiene (DCPD) and chemically attached to polydicyclopentadiene (PDCPD) through ROMP copolymerization with an industrial DCPD formulation. The resulting materials have been subjected to thermal ageing studies and their behavior was compared with a 2,6-di-*tert*-butyl-4-methylphenol (BHT)-stabilized bulk PDCPD.

## 2. Experimental

### 2.1. General Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC-400 spectrometer operating at 400.16 MHz for <sup>1</sup>H NMR and 100.62 MHz for <sup>13</sup>C NMR. The coupling constants and chemical shifts are reported in hertz (Hz) and parts per million (ppm) relative to deuterated solvent resonances, respectively. High resolution mass spectra (HR-MS) were recorded on a Waters-Micromass® GCT Premier™ (GC, Cl<sup>+</sup>, methane) instrument using a HP 6890 GC apparatus equipped with a chromatographic column of 25 m height, 250 mm diameter, and 0.25 mm thickness. The sample was warmed at a temperature of 40°C for 5 min and then fur-

ther heated up to 220°C at a heating rate of 10°C.min<sup>-1</sup>. The molar masses (number-average molar mass  $\overline{M}_n$ , weight-average molar mass  $\overline{M}_w$ ) and dispersity ( $D = \overline{M}_w/\overline{M}_n$ ) values were measured by Size Exclusion Chromatography (SEC) using tetrahydrofuran (THF) as an eluent, and carried out using a system equipped with a Waters 2707 autosampler, with a guard column (Waters, Styragel, 20 μm Guard column, 30 × 4.6 mm) followed by two columns (Waters, 2 Styragel THF HR2+HR4, 300 × 7.8 mm) and with a Waters RI-2414 detector. The instrument operated at a flow rate of 1.0 mL.min<sup>-1</sup> at 35°C and was calibrated with narrow linear polystyrene (PS) standards ranging in molar mass from 580 g mol<sup>-1</sup> to 483 000 g mol<sup>-1</sup>. Fourier Transform Infra-Red (FT-IR) spectra were obtained using a Nicolet avatar 370 DTGS system. Spectra were obtained at regular time intervals in the MIR region of 4000-500 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> (640 scans) and analyzed using OMNIC Spectra software. Onset oxidation temperature (OOT) was measured by differential scanning calorimetry (DSC) on a TA Instruments Q100 according to already reported procedures [32–34]. A sample of 2.5 mg was placed in an aluminum pan. After placing the uncovered sample pan together with an empty pan reference in a calibrated DSC oven, the sample and the reference were continuously heated at 15°C.min<sup>-1</sup> under pure oxygen gas flow (50 mL.min<sup>-1</sup>). OOT was determined by the onset of the decomposition process characterized by an exothermic peak shown by the DSC in the heat flow.

### 2.2. Materials

All the reagents used in this study were purchased from Sigma-Aldrich, unless otherwise noted. *o*-Dichlorobenzene (99%), dicyclopentadiene formulation (DCPD, TELENE SAS), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC.HCl, ≥98%), 4-(*N,N*-dimethylamino)pyridine (DMAP, 99%), 3,5-di-*tert*-butyl-4-hydroxybenzoic acid (98%), 3,5-di-*tert*-butyl-4-hydroxyphenylpropanoic acid (≥98%, Fisher Chemical), 2,6-di-*tert*-butyl-4-methylphenol (BHT, ≥ 99%), ethyl vinyl ether (99%, Acros), 2-hydroxyethyl-5-norbornene-2-carboxylate (Molekula), magnesium sulfate (MgSO<sub>4</sub>, Fisher Chemical), polypropylene (PP, isotactic,  $\overline{M}_w \sim 12\ 000\ \text{g mol}^{-1}$ , average  $\overline{M}_n \sim 5\ 000\ \text{g mol}^{-1}$ ), ruthenium salicylaldehyde phenylindenyldiene complex (TELENE SAS), silicagel for column chromatography (SiO<sub>2</sub>, Kieselgel

60, 230-400 mesh Merck), sodium bicarbonate ( $\text{NaHCO}_3$ , Fisher Chemical) and sodium chloride ( $\text{NaCl}$ , grade technical grade, Fisher Chemical) were used as received. Pure water was obtained from a reverse-osmosis purification system and had a conductivity of  $18.2 \text{ M}\Omega \text{ cm}$  at  $25^\circ \text{C}$ . Dichloromethane (DCM, HPLC grade, Fisher Chemical) was dried over a dry solvent station GT S100. Cyclohexane (99.8%, Quaron), ethyl acetate (EtOAc, technical grade), diethyl ether (technical grade), and methanol (technical grade) were freshly distilled before use. 2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)acetic acid [28, 35] and (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro-(phenylmethylene)bis(pyridine)ruthenium [36] (**G3'**) were synthesized according to a literature procedure.

### 2.3. Synthesis of 2-((3,5-di-*tert*-butyl-4-hydroxybenzoyl)oxy)ethyl 5-norbornene-2-carboxylate (**M1**) and 2-((3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propanoyl)oxy)ethyl 5-norbornene-2-carboxylate (**M2**)

3,5-Di-*tert*-butyl-4-hydroxybenzoic acid (for **M1**) or 3,5-di-*tert*-butyl-4-hydroxyphenylpropanoic acid (for **M2**) (6.04 mmoles), EDC.HCl (1.1573 g, 6.04 mmoles) and DMAP (67.1 mg, 0.55 mmole) were dissolved in dry DCM (10 mL) in a 50 mL round-bottom flask equipped with a magnetic stirrer and a rubber septum. The solution was kept stirring for 5 min. A solution of 2-hydroxyethyl-5-norbornene-2-carboxylate (1.000 g, 5.49 mmoles) in 10 mL of dry DCM was added dropwise under argon at  $0^\circ \text{C}$ . The resulting mixture was kept stirring overnight at room temperature. The reaction mixture was washed with  $\text{NaHCO}_3$  solution (0.1N), deionized water and brine. The organic layer was dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed under reduced pressure.

**M1.** The crude product was purified by chromatography on  $\text{SiO}_2$  using 5/2 cyclohexane/ EtOAc as the eluent. The product was dried for overnight resulting in the pure product (1.3427 g; 59%) as a yellow solid.  $^1\text{H}$  NMR (400.16 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 7.91 (s, 2H,  $H_{\text{Ar}}$ ), 6.15 (m, 2H,  $\text{CH}=\text{CH}-\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$  *endo* and *exo*), 6.09 (dd,  $^3J = 5.2 \text{ Hz}$ ,  $^3J = 2.8 \text{ Hz}$ , 1H,  $\text{CH}=\text{CH}-\text{CH}-\text{CH}_2$  *exo*), 5.92 (dd,  $^3J = 5.6 \text{ Hz}$ ,  $^3J = 2.8 \text{ Hz}$ , 1H,  $\text{CH}=\text{CH}-\text{CH}-\text{CH}_2$  *endo*), 5.69 (s, 1H, OH), 4.64-4.29 (m, 4H,  $\text{C}(\text{O})\text{O}-\text{CH}_2-\text{CH}_2$ ), 3.22 (s, 1H,  $\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$  *endo*), 3.06 (s, 1H,  $\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$  *exo*), 2.98 (dt,  $^3J = 12 \text{ Hz}$ ,  $^3J = 4 \text{ Hz}$ , 1H,  $\text{CH}-\text{C}(\text{O})\text{O}$  *endo*), 2.90 (s, 1H,  $\text{CH}_2$  *bridge-CH-CH}\_2), 2.26 (ddd,  $^3J = 12 \text{ Hz}$ ,  $J = 4 \text{ Hz}$ ,  $^3J = 1.2 \text{ Hz}$ , 1H,  $\text{CH}-\text{C}(\text{O})\text{O}$  *exo*), 1.94 (m, 1H,  $\text{CHH}-\text{CH}-\text{C}(\text{O})$  *endo* and *exo*), 1.54-1.26 (m, 21H,  $-\text{C}(\text{CH}_3)_3$ ,  $\text{CHH}-\text{CH}-\text{C}(\text{O})$  *endo* and *exo*,  $\text{CH}_2$  *bridge*) (Fig. S1).  $^{13}\text{C}$  NMR (100.62 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 174.06 ( $\text{CH}-\text{C}(\text{O})\text{O}$ ), 166.83 ( $\text{CH}_2-\text{OC}(\text{O})$ ), 158.37 (C-OH), 137.82 ( $\text{CH}=\text{CH}-\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$ ), 135.7 (C-C( $\text{CH}_3$ ) $_3$ ), 132.05 ( $\text{CH}=\text{CH}-\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$ ), 127.36 ( $\text{CH}_{\text{Ar}}$ ), 120.86 ( $\text{CH}_2-\text{OC}(\text{O})-\text{C}_{\text{Ar}}$ ), 62.35 ( $\text{CH}-\text{C}(\text{O})\text{O}-\text{CH}_2$ ), 62.09 ( $\text{CH}_2-\text{OC}(\text{O})-\text{Ar}$ ), 49.48 ( $\text{CH}_2$  *bridge*), 45.46 ( $=\text{CH}-\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$ ), 43.30 ( $=\text{CH}-\text{CH}-\text{CH}_2$ ), 42.52 ( $\text{CH}-\text{C}(\text{O})\text{O}$ ), 36.35 (C( $\text{CH}_3$ ) $_3$ ), 29.77 (C( $\text{CH}_3$ ) $_3$ ), 28.82 ( $\text{CH}_2-\text{CH}-\text{C}(\text{O})\text{O}$ ) (Fig. S2). FT-IR ( $\text{cm}^{-1}$ ): 3562 ( $\nu$  O-H), 2958 ( $\nu$  C-H alkane), 1711 ( $\nu$  C=O ester), 1431 ( $\delta$  C-H alkane), 1300, 1227 ( $\nu$  C-O ester), 1184, 1110, 764, 710 ( $\gamma$  C-H alkene). HRMS ( $\text{Cl}-\text{Na}^+$ ): Calcd for  $\text{C}_{25}\text{H}_{34}\text{O}_5+\text{Na}^+$ : 437.2304; found: 437.2282.*

**M2.** The crude product was purified by chromatography on  $\text{SiO}_2$  using 8/2 cyclohexane/ EtOAc as the eluent. The product was dried for overnight resulting in the pure product (1.3613 g; 56%) as a brown viscous oil.  $^1\text{H}$  NMR (400.16 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 6.99 (s, 2H,  $\text{CH}_{\text{Ar}}$ ), 6.18 (dd,  $^3J = 8 \text{ Hz}$ ,  $^3J = 4 \text{ Hz}$ , 1H,  $\text{CH}=\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$  *endo*), 6.14 (dd,  $^3J = 8 \text{ Hz}$ ,  $^3J = 4 \text{ Hz}$ ,  $\text{CH}=\text{CH}-\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$  *exo*), 6.10 (dd,  $^3J = 8 \text{ Hz}$ ,  $^3J = 4 \text{ Hz}$ , 1H,  $\text{CH}=\text{CH}-\text{CH}-\text{CH}_2$  *exo*), 5.92 (dd,  $^3J = 8 \text{ Hz}$ ,  $^3J = 4 \text{ Hz}$ , 1H,  $\text{CH}=\text{CH}-\text{CH}-\text{CH}_2$  *endo*), 5.08 (s, 1H, OH), 4.44-4.11 (m, 4H,  $\text{C}(\text{O})\text{O}-\text{CH}_2-\text{CH}_2-\text{OC}(\text{O})$ ), 3.21 (s, 1H,  $=\text{CH}-\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$  *endo*), 3.04 (s, 1H,  $=\text{CH}-\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$  *exo*), 2.97 (dt,  $^3J = 8 \text{ Hz}$ ,  $^3J = 4 \text{ Hz}$ , 1H,  $\text{CH}-\text{C}(\text{O})\text{O}$  *endo*), 2.88 (m, 3H,  $\text{CH}_2$  *bridge-CH-CH}\_2,  $\text{OC}(\text{O})-\text{CH}_2-\text{CH}_2-\text{Ar}$ ), 2.62 (t,  $J = 8 \text{ Hz}$ , 2H,  $\text{OC}(\text{O})-\text{CH}_2-\text{CH}_2-\text{Ar}$ ), 2.26 (dd,  $J = 12 \text{ Hz}$ ,  $J = 4 \text{ Hz}$ , 1H,  $\text{CH}-$*

$\text{C}(\text{O})\text{O}$  *exo*), 1.91 (m, 1H,  $\text{CHH}-\text{CH}-\text{C}(\text{O})$  *endo* and *exo*), 1.51-1.19 (m, 21H, C( $\text{CH}_3$ ) $_3$ ,  $\text{CHH}-\text{CH}-\text{C}(\text{O})$  *endo* and *exo*,  $\text{CH}_2$  *bridge*) (Fig. S3).  $^{13}\text{C}$  NMR (100.62 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 175.94 ( $\text{CH}-\text{C}(\text{O})\text{O}$ ), 174.41 ( $\text{CH}_2-\text{OC}(\text{O})$ ), 152.22 (C-OH), 137.77 ( $\text{CH}=\text{CH}-\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$ ), 135.79 (C-C( $\text{CH}_3$ ) $_3$ ), 132.20 ( $\text{CH}=\text{CH}-\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$ ), 130.99 ( $\text{CH}_{\text{Ar}}$ ), 124.78 ( $\text{CH}-\text{C}-\text{C}(\text{CH}_3$ ) $_3$ ), 62.51 ( $\text{CH}-\text{C}(\text{O})\text{O}-\text{CH}_2$ ), 61.88 ( $\text{CH}_2-\text{OC}(\text{O})$ ), 49.49 ( $\text{CH}_2$  *bridge*), 46.72 ( $\text{CH}_2$  *bridge-CH-CH}-\text{C}(\text{O})\text{O}), 46.27 ( $\text{CH}_2$  *bridge-CH-CH}\_2), 45.75 ( $\text{CH}-\text{C}(\text{O})\text{O}$ ), 36.09 ( $\text{OC}(\text{O})\text{CH}_2-\text{CH}_2-\text{Ar}$ ), 34.22 (C( $\text{CH}_3$ ) $_3$ ), 31.42 ( $\text{OC}(\text{O})\text{CH}_2-\text{CH}_2-\text{Ar}$ ), 30.18 (C( $\text{CH}_3$ ) $_3$ ), 29.21 ( $\text{CH}_2-\text{CH}-\text{C}(\text{O})\text{O}$ ) (Fig. S4). FT-IR ( $\text{cm}^{-1}$ ): 3630 ( $\nu$  O-H), 2950 ( $\nu$  C-H alkane), 1730 ( $\nu$  C=O ester), 1433 ( $\delta$  C-H alkane), 1149, 710 ( $\gamma$  C-H alkene). HRMS ( $\text{Cl}-\text{Na}^+$ ): Calcd. for  $\text{C}_{27}\text{H}_{38}\text{O}_5+\text{Na}^+$ : 465.2617; found: 465.2616.**

### 2.4. Synthesis of 2-(2-(3,5-di-*tert*-butyl-4-hydroxyphenoxy)acetoxy)ethyl 5-norbornene-2-carboxylate (**M3**)

2-(3,5-Di-*tert*-butyl-4-hydroxyphenoxy)acetic acid (0.8186 g, 2.92 mmoles), EDC.HCl (0.5649 g, 2.96 mmoles) and DMAP (33.6 mg, 0.27 mmole) were dissolved in dry DCM (5 mL) in a 50 mL round-bottom flask equipped with a magnetic stirrer and a rubber septum. The solution was kept stirring for 5 min. A solution of 2-hydroxyethyl-5-norbornene-2-carboxylate (0.500 g; 2.75 mmoles) in 5 mL of dry DCM was added dropwise under argon at  $0^\circ \text{C}$ . The resulting mixture was kept stirring overnight at room temperature. The reaction mixture was washed with  $\text{NaHCO}_3$  solution (0.1N), deionized water and brine. The organic layer was dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. The crude product was purified by chromatography on  $\text{SiO}_2$  using 9/1 cyclohexane/ EtOAc as the eluent. The product was dried for overnight resulting in the pure product (0.6227 g; 51%) as an orange-brown viscous oil.  $^1\text{H}$  NMR (400.16 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 6.78 (s, 2H,  $\text{CH}_{\text{Ar}}$ ), 6.17 (m, 3H,  $\text{CH}=\text{CH}-\text{CH}_2$  *endo*,  $\text{CH}=\text{CH}-\text{CH}-\text{CH}_2$  *exo*,  $\text{CH}=\text{CH}-\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$  *endo*), 5.92 (dd, 1H,  $^3J = 8 \text{ Hz}$ ,  $^3J = 4 \text{ Hz}$ ,  $\text{CH}=\text{CH}-\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$  *exo*), 4.83 (s, 1H, OH), 4.59 (s, 1H,  $-\text{C}(\text{O})\text{O}-\text{CH}_2-\text{O}$ ), 4.49-4.12 (m, 4H,  $\text{C}(\text{O})\text{O}-\text{CH}_2-\text{CH}_2-\text{OC}(\text{O})$ ), 3.19 (s, 1H,  $=\text{CH}-\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$  *endo*), 3.00 (s, 1H,  $=\text{CH}-\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$  *exo*), 2.98 (dd,  $^3J = 8 \text{ Hz}$ ,  $^3J = 4 \text{ Hz}$ , 1H,  $\text{CH}-\text{C}(\text{O})\text{O}$  *endo*), 2.91 (m, 2H,  $\text{CH}_2$  *bridge-CH-CH}\_2), 2.25 (dd,  $^3J = 12 \text{ Hz}$ ,  $^3J = 4 \text{ Hz}$ , 1H,  $\text{CH}-\text{C}(\text{O})\text{O}$  *exo*), 1.90 (m, 1H,  $=\text{CH}-\text{CH}-\text{CHH}-\text{CH}-\text{C}(\text{O})$  *endo* and *exo*), 1.55-1.17 (m, 21H, C( $\text{CH}_3$ ) $_3$ ,  $=\text{CH}-\text{CH}-\text{CHH}-\text{CH}-\text{C}(\text{O})$  *endo* and *exo*,  $\text{CH}_2$  *bridge*) (Fig. S5).  $^{13}\text{C}$  NMR (100.62 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 174.67 ( $\text{CH}-\text{C}(\text{O})\text{O}$ ), 168.98 ( $\text{CH}_2-\text{OC}(\text{O})$ ), 150.72 (C-OH), 148.30 (O- $\text{C}_{\text{Ar}}$ ), 138.04 ( $\text{CH}=\text{CH}-\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$ ), 135.45 (C-C( $\text{CH}_3$ ) $_3$ ), 131.51 ( $\text{CH}=\text{CH}-\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$ ), 111.74 ( $\text{CH}_{\text{Ar}}$ ), 65.78 ( $\text{OC}(\text{O})-\text{CH}_2-\text{O}$ ), 63.15 (C(O)-O- $\text{CH}_2$ ), 61.39 ( $\text{CH}_2-\text{CH}_2-\text{OC}(\text{O})$ ), 50.05 ( $\text{CH}_2$  *bridge*), 45.72 ( $=\text{CH}-\text{CH}-\text{CH}-\text{C}(\text{O})\text{O}$ ), 43.11 ( $=\text{CH}-\text{CH}-\text{CH}_2$ ), 42.52 ( $\text{CH}-\text{C}(\text{O})\text{O}$ ), 34.46 (C( $\text{CH}_3$ ) $_3$ ), 30.16 (C( $\text{CH}_3$ ) $_3$ ), 28.95 ( $\text{CH}-\text{CH}_2-\text{CH}-\text{C}(\text{O})\text{O}$ ) (Fig. S6). FT-IR ( $\text{cm}^{-1}$ ): 3634 ( $\nu$  O-H), 2952 ( $\nu$  C-H alkane), 1730 ( $\nu$  C=O ester), 1428 ( $\delta$  C-H alkane), 1168, 1096, 710 ( $\gamma$  C-H alkene). HRMS ( $\text{Cl}-\text{Na}^+$ ): Calcd. for  $\text{C}_{26}\text{H}_{36}\text{O}_6 + \text{Na}^+$ : 467.2410; found: 467.2389.*

### 2.5. General procedure for the ROMP of hindered phenol-containing norbornenyl monomers

In a typical experiment, a dry Schlenk tube was charged with the desired quantity of monomer and a stir bar. The Schlenk tube was capped with a rubber septum, and the desired quantity of degassed anhydrous DCM by freeze-pump-thaw cycles was added via a syringe to obtain a homogeneous solution ( $[\text{monomer}]_0 = 0.05 \text{ mol}\cdot\text{L}^{-1}$ ). The Schlenk tube was immersed in an oil bath pre-set at  $25^\circ \text{C}$  and was stirred under argon for 10 min. A stock solution of catalyst **G3'** in degassed anhydrous DCM ( $[\text{G3'}]_0 = 5-7 \text{ mmol}\cdot\text{L}^{-1}$ ) was prepared in a separate vial. The desired quantity of catalyst **G3'** was injected quickly into the monomer solution to initiate the polymerization (initial reaction time,  $t = 0$ ). The reaction mixture was stirred from 8 min to 1h30. Aliquots of

**Table 1**

Characteristics of the polymers obtained from ROMPs of hindered phenol-containing norbornenyl monomers in DCM at 25°C, using **G3'** initiator with varying monomer-to-initiator molar ratio.

Run	Monomer	$[M]_0/[I]_0^{a)}$	Reaction time (min)	Conv. <sup>b)</sup> (%)	$\overline{M}_{n,calc}^{c)}$ (g.mol <sup>-1</sup> )	$\overline{M}_{n,SEC}^{d)}$ (g.mol <sup>-1</sup> )	$D^{d)}$
1	<b>M1</b>	100	10	100	41 500	38 300	1.09
2	<b>M1</b>	500	15	100	207 100	108 500	1.34
3	<b>M1</b>	1000	90	100	414 100	200 700	1.51
4	<b>M2</b>	100	8	100	44 300	53 600	1.54
5	<b>M2</b>	500	20	83	183 530	121 400	1.68
6	<b>M2</b>	1000	90	78	344 860	202 600	1.79
7	<b>M3</b>	100	8	99	44 060	31 400	1.13
8	<b>M3</b>	100	10	100	44 500	48 400	1.90
9	<b>M3</b>	500	20	97	215 440	120 600	1.47
10	<b>M3</b>	1000	90	93	413 020	233 000	1.87

<sup>a)</sup> Monomer-to-initiator molar ratio. <sup>b)</sup> The monomer conversions were determined by comparing the integrations of the alkene protons of hindered phenol-containing norbornenes (**M1**: 5.92-6.15 ppm, **M2**: 5.92-6.18 ppm, **M3**: 5.92-6.17 ppm) and the aromatic protons of the monomers (**M1**: 7.91 ppm, **M2**: 6.99 ppm, **M3**: 6.78 ppm) and their polymer (**PM1**: 7.87 ppm, **PM2**: 6.98 ppm, **PM3**: 6.76 ppm) from <sup>1</sup>H NMR spectra of the crude mixtures. <sup>c)</sup>  $\overline{M}_{n,calc} = ([M]_0/[I]_0) \times \text{conv.} \times M_{monomer} + M_{extr.}$  with **M1** = 414 g mol<sup>-1</sup>, **M2** = 442 g mol<sup>-1</sup>, **M3** = 444 g.mol<sup>-1</sup>, and  $M_{extr.} = 104$  g.mol<sup>-1</sup>. <sup>d)</sup> Determined by SEC in tetrahydrofuran (THF) using a RI detector, calibrated with linear polystyrene (PS) standards.

reaction mixture were taken at different reaction times and polymerizations were quenched by adding two drops of ethyl vinyl ether for <sup>1</sup>H NMR spectroscopy analysis. The solvent of aliquots was then removed under reduced pressure for further SEC measurements to determine number-average molar masses ( $\overline{M}_{n,SEC}$ ) and dispersity ( $D$ ). The final reaction mixture was then diluted in DCM and precipitated into 20 mL of stirred cold methanol, filtered and dried overnight under reduced pressure. The recovered polymer was then analyzed by <sup>1</sup>H NMR spectroscopy and SEC.

**Poly[2-((3,5-di-tert-butyl-4-hydroxybenzoyl)oxy)ethyl 5-norbornene-2-carboxylate] (PM1).** Yellow solid.  $[M1]_0/[G3']_0 = 100$  (run 1, Table 1); conversion = 100 %,  $\overline{M}_{n,SEC} = 38\,300$  g.mol<sup>-1</sup>;  $D = 1.09$ . <sup>1</sup>H NMR (400.16 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.87 (bs, 2nH, CH<sub>Ar</sub>), 5.99 (bs, 1nH, OH), 5.50-5.00 (bs, 2nH, CH=CH), 4.50-4.00 (bs, 4nH, CH<sub>2</sub>-CH<sub>2</sub>), 3.25-2.20 (bs, 3nH, CH-CH-C(O)O, =CH-CH-CH<sub>2</sub>), 1.90 (bs, 2nH, CH<sub>2</sub>-CH-C(O)), 1.54-1.26 (bs, 20nH, C(CH<sub>3</sub>)<sub>3</sub>, CH<sub>2</sub> bridge) (Fig. S7).

**Poly[2-((3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoyl)oxy)ethyl 5-norbornene-2-carboxylate] (PM2).** Pale orange solid.  $[M2]_0/[G3']_0 = 100$  (run 4, Table 1); conversion = 100 %,  $M_{n,SEC} = 53\,600$  g.mol<sup>-1</sup>;  $D = 1.54$ . <sup>1</sup>H NMR (400.16 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 6.98 (bs, 2nH, CH<sub>Ar</sub>), 5.08 (bs, 1nH, OH), 5.20-5.50 (bs, 2nH, CH=CH), 4.35-4.00 (bs, 4nH, C(O)O-CH<sub>2</sub>-CH<sub>2</sub>-O(CO)), 3.34-2.70 (bs, 2nH, =CH-CH-CH-C(O)O, CH-CH-CH<sub>2</sub>, OC(O)-CH<sub>2</sub>-CH<sub>2</sub>-Ar), 2.62 (t,  $J = 12$  Hz, 4nH, OC(O)-CH<sub>2</sub>-CH<sub>2</sub>-Ar), 1.91 (bs, 2nH, =CH-CH<sub>2</sub>-CH-C(O)), 1.51-1.19 (bs, 20nH, C(CH<sub>3</sub>)<sub>3</sub>, CH<sub>2</sub> bridge) (Fig. S8).

**Poly[2-(2-(3,5-di-tert-butyl-4-hydroxyphenoxy)acetoxy)ethyl 5-norbornene-2-carboxylate] (PM3).** Translucent solid.  $[M3]_0/[G3']_0 = 100$  (run 7, Table 1); conversion = 99 %,  $M_{n,SEC} = 31\,400$  g.mol<sup>-1</sup>;  $D = 1.13$ . <sup>1</sup>H NMR (400.16 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 6.76 (bs, 2nH, CH<sub>Ar</sub>), 5.50-5.00 (bs, 2nH, CH=CH), 4.85 (1nH, OH), 4.58 (bs, 2nH, C(O)O-CH<sub>2</sub>-O), 4.50-4.00 (bs, 4nH, CH<sub>2</sub>-CH<sub>2</sub>), 3.25-2.25 (bs, 3nH, CH-CH-C(O)O, =CH-CH-CH<sub>2</sub>), 1.90 (bs, 2nH, =CH-CH-CH<sub>2</sub>-CH-C(O)), 1.50-1.25 (bs, 20nH, C(CH<sub>3</sub>)<sub>3</sub>, CH<sub>2</sub> bridge) (Fig. S9).

## 2.6. General procedure for preparation of PP and PP/hindered phenol-containing polynorbornene blends

All samples are prepared according to a procedure adapted from the literature [29]. In a typical experiment, a 100 mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser was charged with 1 g of PP with 15 mL of *o*-dichlorobenzene. A solution of hindered phenol-containing polynorbornene of  $\overline{DP}_n = 100$  (5  $\mu$ mol in di-*tert*-butylphenol func-

tions) in 1 mL of DCM was prepared. 0.4 mL of the solution (2  $\mu$ mol in di-*tert*-butylphenol functions) was added to the round-bottom flask under nitrogen atmosphere. The mixture was stirred at 135°C for 1 hour to dissolve PP completely. For PP and PP/hindered phenol-containing polynorbornene, the mixture was cooled and precipitated into 100 mL of stirred cold diethyl ether, then the blend was filtered and dried overnight at 70°C under reduced pressure.

## 2.7. General procedure for preparation of PDCPD films and exposure conditions

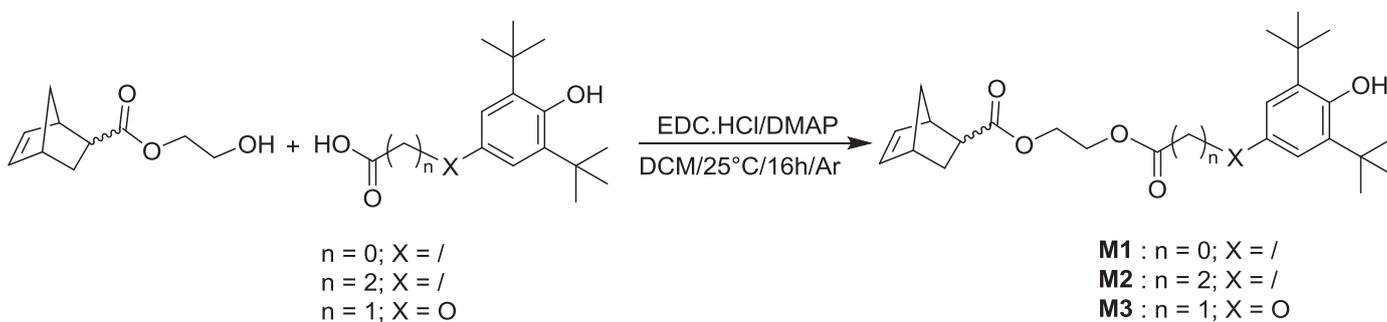
In a typical experiment, stabilized bulk PDCPD materials were prepared in a 100 mL plastic beaker by mixing 10 g of DCPD formulation purchased by TELENE SAS and the desired quantity of BHT, hindered phenol-containing norbornene or polynorbornene (1.044 mmole/100 g of DCPD formulation). 0.1 g of a solution of the ruthenium salicylaldimine phenylindenyldiene complex purchased by TELENE SAS was then added to the mixture. The polymerization occurs immediately at room temperature in 10 min. After polymerization, material was cut in 15-25  $\mu$ m slices using a Reichert Jung microtome. Samples were stored in the freezer prior to exposure in ventilated ovens at atmospheric pressure at 50°C.

## 3. Results and discussion

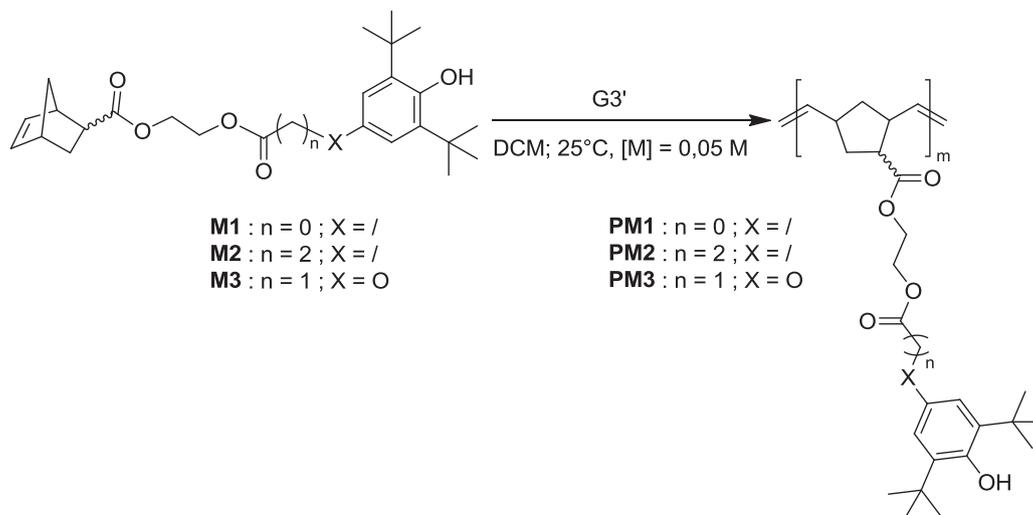
### 3.1. Synthesis of hindered phenol-based norbornenyl monomers

A series of hindered phenol-containing norbornenyl monomers were synthesized from the 2-hydroxyethyl-5-norbornene-2-carboxylate (**M1**, **M2** and **M3**, Scheme 2). For the latter, the electron-donating effect of the oxygen atom located in the *para*-position of phenol was reported to improve the efficiency of the antioxidant group [31]. The new **M1** and **M3** monomers were obtained by esterification in a one-step process from 2-hydroxyethyl-5-norbornene-2-carboxylate (*endo/exo* = 80:20) and the 3,5-di-*tert*-butyl-4-hydroxybenzoic acid and the 2-(3,5-di-*tert*-butyl-4-hydroxyphenoxy)acetic acid [35], respectively. Monomer **M2** [37] was synthesized through a new procedure by esterification with 3,5-di-*tert*-butyl-4-hydroxyphenylpropanoic acid.

The <sup>1</sup>H NMR spectra of **M1** (Fig. S1), **M2** (Fig. S3) and **M3** (Fig. S5) showed the signals of CH=CH protons at 5.90 and 6.20 ppm (labeled *a*<sub>exo</sub>, *a*<sub>endo</sub>, *b*<sub>endo</sub> and *b*<sub>exo</sub>, Fig. S1, S3 and S5) and the presence of two multiplets attributed to -O-CH<sub>2</sub>-CH<sub>2</sub>-O- at 4.29 and 4.64 ppm, 4.11 and 4.44 ppm, and 4.12 and 4.49 ppm for **M1**, **M2**,



**Scheme 2.** Synthesis of hindered phenol-containing norbornenyl monomers **M1**, **M2** and **M3**.



**Scheme 3.** ROMP of hindered phenol-containing norbornenyl monomers **M1**, **M2** and **M3**.

and **M3** (labeled h and i, Fig. S1, S3 and S5), respectively. The integration area ratio of the characteristic resonances is in good agreement with the ratio of corresponding protons, demonstrating that full esterification occurred. The *endo/exo* ratio was preserved after esterification and purification, as ascertained by the integration area ratios of the vinylic protons (labeled  $a_{exo}$ ,  $a_{endo}$ ,  $b_{endo}$  and  $b_{exo}$ , Fig. S1, S3 and S5) and a vinylic *endo* proton (labeled  $b_{endo}$ , Fig. S1, S3 and S5). Moreover, HRMS analyses confirmed the structure of **M1**, **M2** and **M3** as the experimental molecular weights ( $M + Na^+ = 437.2282$ ,  $465.2616$  and  $467.2389$  respectively) were in good agreement with the calculated values ( $M + Na^+ = 437.2004$ ,  $465.2617$  and  $467.2410$  respectively).

### 3.2. ROMP of hindered phenol-based norbornenyl monomers

**M1**, **M2** and **M3** were polymerized in dichloromethane (DCM) at 25°C through ring-opening metathesis polymerization (ROMP) using Grubbs' third-generation catalyst (**G3'**) as the initiator, possessing dramatic tolerance toward various functional groups of substrates [38] (Scheme 3).

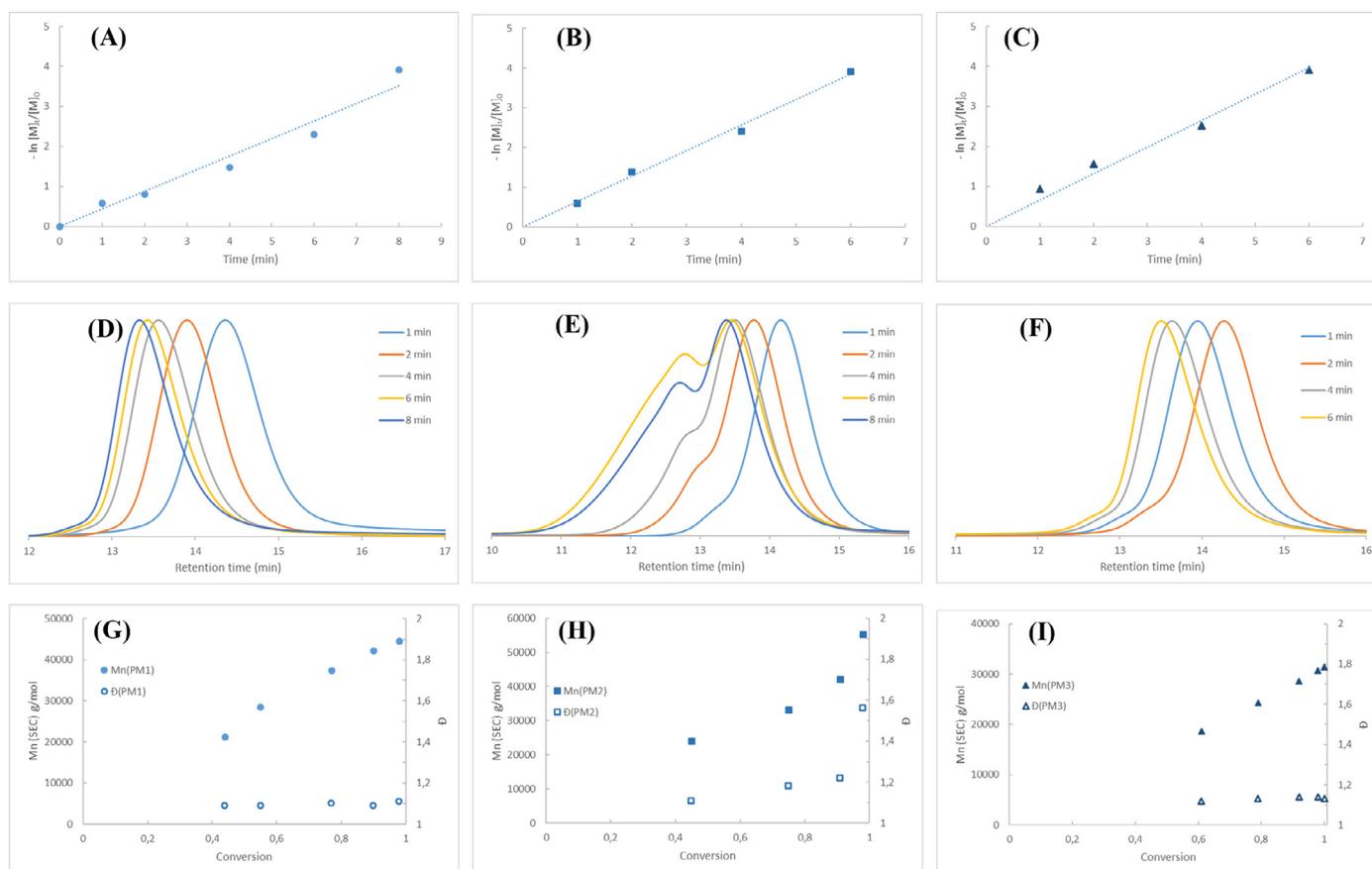
ROMP of the hindered phenol-containing norbornenyl monomers was conducted at increasing monomer-to-initiator molar ratio  $[M]_0/[I]_0$  (100–1000). The conversion, number-average molar mass ( $\overline{M}_{n,SEC}$ ), and dispersity ( $\mathcal{D}$ ) are summarized in Table 1.

$\overline{M}_{n,SEC}$  increased with the increase of  $[M]_0/[I]_0$ , and the  $\mathcal{D}$  values were in the range 1.09–1.90. The conversion of the polymerization remained relatively constant throughout the  $[M]_0/[I]_0$  series for **M1** and **M3**. While the SEC traces of the polymers **PM1** and

**PM3** displayed a monomodal distribution with narrow dispersity  $\mathcal{D} < 1.14$  for a  $[M]_0/[I]_0 = 100$  (Fig. S10A and S12A), SEC traces for  $[M]_0/[I]_0$  ratios of 500 and 1000 showed a monomodal mass distribution with a spreading toward lower molar masses due to backbiting [39,40] (Fig. S10B, S10C, S12B and S12C). It should be noted that ROMP of **M3** for a  $[M]_0/[I]_0$  ratio of 100 has to be conducted within 8 min instead of 10 min with **M1**, in order to avoid the apparition of a second population at lower retention times, as ascertained by the SEC trace (Fig. S13B vs. S13A). The ratio of the peak molecular weight  $M_p$  of these two populations ( $45\ 200$  and  $89\ 800\ \text{g mol}^{-1}$ ) of around 2 suggests chains recombination reactions [41]. Unlike **M1** and **M3**, the increase of  $[M]_0/[I]_0$  resulted in a decrease of the conversion of **M2** as well as an increase of the  $\mathcal{D}$  values (runs 4–6, Table 1). The loss of control of the polymerization entailed tailing of the elution profile in the SEC trace (Fig. S11) toward lower molar masses can be attributed to backbiting. Moreover, chains recombination reactions occurred for a  $[M]_0/[I]_0$  ratio of 100 (run 4, Table 1) even for lower conversions (Fig. 1E), showing the ill-defined ROMP of **M2**. The influence of the anchor group between the ROMP-able group and the sterically hindered phenol on the kinetics of ROMP was evaluated.

### 3.3. Influence of the structure of hindered phenol-based norbornenyl monomers on kinetics

Kinetics analysis of ROMP of hindered phenol-containing norbornenyl monomers **M1**, **M2** and **M3** with an initial monomer concentration of  $0.05\ \text{mol.L}^{-1}$  and a  $[M]_0/[I]_0$  ratio of 100 at 25°C in DCM using **G3'** as the initiator were conducted using  $^1\text{H}$



**Fig. 1.** Kinetic plots  $-\ln([M]_t/[M]_0)$  versus reaction time for ROMP using **G3'** as the initiator with an initial monomer concentration of  $0.05 \text{ mol.L}^{-1}$  and a  $[M]_0/[I]_0$  ratio of 100 at  $25^\circ\text{C}$  in DCM of (A) **M1**, (B) **M2**, and (C) **M3**. SEC traces for ROMP of (D) **M1**, (E) **M2**, and (F) **M3**. Molar mass and dispersity versus conversion plots for (G) **M1**, (H) **M2**, and (I) **M3**.

NMR spectroscopy. Linear pseudo first order was observed for the ROMP of the hindered phenol-containing norbornenyl monomers **M1**, **M2** and **M3** (Fig. 1A-C). The SEC chromatograms of the crude polymers at different reaction time during ROMP of **M1** and **M3** (Fig. 1D and 1F) are symmetrical and shift to lower elution volumes with increasing polymerization time. Additional evidence of a well-controlled polymerization is indicated by the linear progression of  $\overline{M}_{n,SEC}$  vs. monomer conversion and the narrow molar mass distribution (Fig. 1G and 1I). In contrast, while the SEC chromatograms of **PM2** shown in Fig. 1E shift to lower elution times, dispersities increase with increasing monomer conversion (Fig. 1H) and a high molar mass shoulder is observed from the very start of the polymerization that is approximately double the molar mass of the main polymer peak. It should be noted that such a behavior was also observed for **PM3** at the end of the polymerization (run 8 vs. run 7, Table 1 and Fig. S13B vs. S13A). These new populations can be attributed to acyclic metathesis between the chain-end and double bonds in the polymer which competes with propagation during ROMP, as reported by Lee *et al.* [41] (Fig. 1E). While the observed coupling for **PM3** is ascribed to prolonged stirring of living propagating polymer species without the addition of ethyl vinyl ether even after complete conversion [42], the competing acyclic metathesis reactions that occur during the polymerization of **PM2** have been reported as the result of the scrambling of chain length between two interacting chains [43]. This side reaction could be minimized by diluting the living end concentration by increasing the monomer-to-initiator ratio under the same initial conditions as observed on the SEC trace for initial monomer-to-initiator ratios of 500 and 1000 (B and C, Fig. S11).

**Table 2**

Kinetic data for ROMP of **M1**, **M2** with **M3** using **G3'** as the initiator with an initial monomer concentration of  $0.05 \text{ mol.L}^{-1}$  and a  $[M]_0/[I]_0$  ratio of 100 at  $25^\circ\text{C}$  in DCM.

Run	Monomer	Conv. % (2 min)	$k_p^{app}$ <sup>a)</sup>	$k_p$ <sup>b)</sup>
1	<b>M1</b>	55	0.384	7.7
2	<b>M2</b>	75	0.640	12.8
3	<b>M3</b>	85	0.670	13.4

<sup>a)</sup>  $\text{min}^{-1}$ , calculated from the slopes of semilogarithmic kinetic plots. <sup>b)</sup>  $\text{min}^{-1}.\text{L.mol}^{-1}$ .

Kinetic analysis of hindered phenol-containing norbornenyl monomers **M1**, **M2** and **M3** with a different anchor group between the ROMP-able entity and the hindered phenol revealed different tendencies in propagation apparent rate constants ( $k_p^{app}$ ) values (Table 2). Electronic effects are minor as the electronic nature of carbonyl oxygen chelating to the Ru center is not changed between **M1**, **M2** and **M3** [30, 44–47]. As stated in Grubbs' works, the much lower reactivity of **M1** ( $0.384 \text{ min}^{-1}$ ) that is two-fold less reactive than **M2** ( $0.640 \text{ min}^{-1}$ ) and **M3** ( $0.670 \text{ min}^{-1}$ ) can be attributed to local steric congestion around the propagating metallocycle or the different solvent quality which may cause the observed difference in the rate of polymerization [48–50].

### 3.4. Stabilizing activity of hindered phenol-containing norbornenes and polynorbornenes

The stabilizing activity of hindered phenol-containing polynorbornenes was evaluated according to a reported procedure by ex-

**Table 3**  
OOT results of PP sample stabilized with **PM1**, **PM2**, and **PM3** hindered phenol-containing polynorbornenes.

Run	Stabilizer	OOT <sup>a)</sup> (°C)
1	-	180 ± 1
2	<b>PM1</b>	189 ± 1
3	<b>PM2</b>	187 ± 1
4	<b>PM3</b>	188 ± 1

<sup>a)</sup> The OOT is reported at the extrapolated onset temperature.

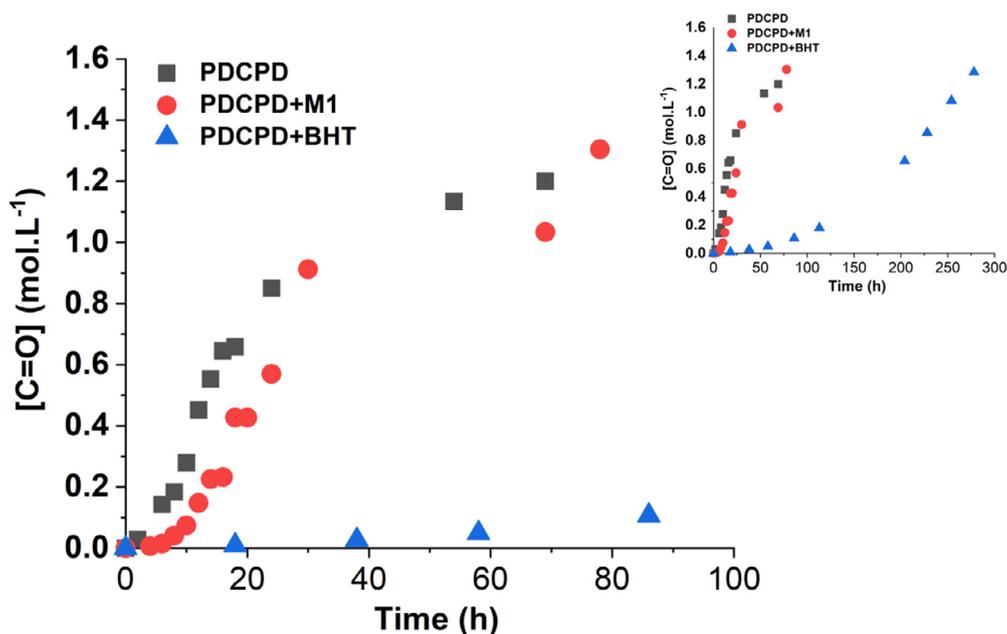
posing virgin polypropylene (PP) and PP stabilized with **PM1**, **PM2** and **PM3** to oxidative conditions [51]. The onset oxidation temperature (OOT) values of PP with hindered phenol-containing polynorbornenes indicate an improved thermal-oxidative stability with respect to pure PP, independently of the nature of the substituent in *para*-position of antioxidant phenol group, which only has a second order influence on antioxidant efficiency (Table 3). The increase in stability is of the same order of magnitude as that already reported in the literature for the hindered phenol-containing polynorbornenes issued from the hindered phenol-containing norbornenes with the R<sub>4</sub> group (Scheme 1) [29].

Further studies on the exploitation of these new antioxidant agents to be used in DCPD formulation for stabilization of PDCPD material have therefore been conducted with (**P**)**M1**. Stabilized bulk PDCPD materials were obtained by bulk polymerization of DCPD formulation using a ruthenium salicylaldimine phenylindenyldiene complex as the initiator in the presence of the stabilizing agent. The concentration of the stabilizing agent has been set at the same concentration as in the industrial formulation (see experimental section) when 2,6-di-*tert*-butyl-4-methylphenol (BHT) is used, i.e. 1.044 mmol in phenol function per 100 g of DCPD formulation. The incorporation of the hindered phenol-based polynorbornenes with a [M]<sub>0</sub>/[I]<sub>0</sub> ratio of 100 failed because of their insolubility in the DCPD formulation.

Incorporation of a hindered phenol-based antioxidant in the PDCPD has then been performed by bulk copolymerization between DCPD and the hindered phenol-containing norbornene **M1** used both as comonomer and stabilizing agent. The thermal ageing of the resulting stabilized bulk PDCPD material (**PDCPD-M1**)

has been studied on 15–25 μm films by Fourier Transform Infra-Red (FT-IR) analysis and compared with a virgin bulk PDCPD film (**v-PDCPD**) and a BHT-stabilized bulk PDCPD film (**PDCPD-BHT**). PDCPD thin films were exposed at 50°C under air. Their oxidation was observed by FT-IR spectroscopy (Fig. S14) with the appearance of absorption peaks, which perfectly overlap for the three **PDCPD** formulations, at around 3400 cm<sup>-1</sup> (highlighted in grey in Fig. S14) ascribed to stretch vibration mode of O-H and at 1650–1750 cm<sup>-1</sup> (highlighted in grey in Fig. S14), ascribed to stretch vibration mode of C=O, the absorptions below 1700 cm<sup>-1</sup> indicating the presence of conjugated carbonyls coming from highly oxidizable allylic carbons [52]. Thermal ageing of the PDCPD films has been monitored by converting carbonyl absorbances into concentrations using Beer Lambert's law with ε<sub>CO</sub> = 300.L.mol<sup>-1</sup> cm<sup>-1</sup> [53] (Fig. 2). The carbonyl concentration of **PDCPD-M1** (B, Fig. 2) displays an induction period of 8 h while **v-PDCPD** (A, Fig. 2) oxidizes instantly. After this induction period, **PDCPD-M1** and **v-PDCPD** oxidize with the same rate, although much faster than **PDCPD-BHT** (C, Fig. 2). Monitoring of thermal ageing of **PDCPD-M1** and **v-PDCPD** is not possible anymore beyond 80 h because the films have become too brittle. While copolymerization between **M1** and DCPD prevents physical loss of antioxidants from the bulk PDCPD material, immobilized phenol is less efficient than its free counterpart. Such a behavior could be induced by the higher hindrance of the carbon in *para*-position of the hindered phenol-containing **M1** compared to BHT, thus limiting the reaction between phenoxy and radicals groups, which is inconsistent with previous works on the efficiency of several phenol groups studied for polyolefin stabilization [54]. These results are more likely due to the low mobility in a glassy polymer [55]. The rate constant for the bimolecular reaction between two peroxy radicals POO° was shown to be much lower than in rubbery materials such as elastomers. It could be the same in particular for the reaction between POO° and radical by products generated by stabilizer. This is in line with the first estimations of corresponding rate constants [56] where the rate constant for POO° + phenoxy radical is about 5 L.mol<sup>-1</sup>.s<sup>-1</sup> at 50°C vs 10<sup>8</sup> in model liquids.

For ageing in aqueous media however, the grafted stabilizers could be more efficient than their free analogs because those latter could migrate out of the polymer.



**Fig. 2.** Carbonyls concentration-time profiles during ageing at 50°C under air of (A) **v-PDCPD**, (B) **PDCPD-M1**, and (C) **PDCPD-BHT**.

## 4. Conclusions

Novel hindered phenol-containing norbornenes were successfully synthesized by esterification between 2-hydroxyethyl-5-norbornene-2-carboxylate and di-*tert*-butyl-4-hydroxy carboxylic acid derivatives. Their subsequent polymerization was performed by ROMP using ruthenium-based third generation initiator **G3**. Well-defined polymers were obtained from **M1** and **M3**. Acyclic metathesis reactions were observed during ROMP of **M2**, which prevent from obtaining well-defined polymers. Kinetics analyses of ROMP for a targeted  $[M]_0/[I]_0$  ratio of 100 show that the norbornene monomer steric congestion plays an important role in the rate of ROMP. The OOT values of PP with the hindered phenol-containing polynorbornenes increased compared to virgin PP, showing their thermo-oxidative resistance. While the incorporation of polynorbornenes as additives in DCPD formulations failed due to their insolubility, hindered phenol-containing norbornene **M1** has been successfully copolymerized with DCPD. The resulting material shows an induction period before its thermal ageing at 50°C monitored by FT-IR analyses.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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