Electronic Supporting Information

for

**N-acetoxy-phthalimide (NAPI) as new H-abstractioning agent at high temperature: application to the melt functionalization of polyethylene**

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1. DFT Calculations
2. Materials
3. TGA analyses
4. NAPI/PE experiments
5. NAPI/TEMPO/PE experiments
6. NAPI/MA/PE experiments
1. DFT Calculations

All the calculations were carried out using the GAUSSIAN 09\textsuperscript{1} software. The geometries of all species were optimized at the B3LYP/6-31G(d) level of theory. The nature of each stationary point was established by B3LYP/6-31G(d) frequency calculations. Enthalpies were calculated using single-point energies obtained at the G3(MP2)-RAD level of theory.

Cartesian coordinates (Å) of B3LYP/6-31G(d) geometries and G3(MP2)-RAD enthalpies at 298.15K in a.u.

**Acyl-TEMPO**

\[
\begin{array}{cccc}
C & -0.007659 & 0.007042 & 0.010827 \\
C & -0.004104 & 0.019807 & 1.541061 \\
C & 1.437971 & 0.007022 & 2.052967 \\
C & 2.295561 & 1.172715 & 1.505729 \\
C & 0.793494 & 1.172736 & -0.616135 \\
H & 1.466721 & 0.047175 & 3.148988 \\
H & -0.542432 & 0.896821 & 1.922152 \\
H & -0.542065 & -0.857298 & 1.921874 \\
H & 0.431465 & -0.937330 & -0.336171 \\
H & -1.031828 & 0.047211 & -0.380537 \\
H & 1.911174 & -0.937351 & 1.754110 \\
N & 2.141935 & 1.138602 & 0.021892 \\
O & 2.901512 & 2.257684 & -0.515803 \\
C & 3.774929 & 0.868135 & 1.813115 \\
H & 4.419113 & 1.719448 & 1.570179 \\
H & 3.895549 & 0.657385 & 2.881884 \\
H & 4.114046 & 0.003559 & 1.236568 \\
C & 1.922258 & 2.510759 & 2.184828 \\
H & 2.284576 & 2.507423 & 3.219444 \\
C & 2.395246 & 3.349805 & 1.667020 \\
H & 0.845649 & 2.691887 & 2.217089 \\
C & 0.028945 & 2.510787 & -0.489722 \\
H & 0.674521 & 3.349830 & -0.763728 \\
H & -0.826452 & 2.507468 & -1.175289 \\
H & -0.359279 & 2.691904 & 0.514973 \\
C & 0.995227 & 0.868175 & -2.113577 \\
H & 0.027291 & 0.657443 & -2.582537 \\
\end{array}
\]
H(G3(MP2)-RAD) = -635.911499

Tempo nitroxide
Acyl radical

H(G3(MP2)-RAD) = -482.857025

TempoN aminyl radical

H(G3(MP2)-RAD) = -152.951904
H(G3(MP2)-RAD) = -407.717804

Acyloxyl radical

H(G3(MP2)-RAD) = -228.103912

N-Acetoxy phthalimide (NAPI)
C     0.017495     0.015296     0.000646
C     0.017440     0.015492     1.400526
C     1.200157     -0.010271     2.124002
C     2.400100     -0.034622     1.400763
C     2.400152     -0.034909     0.000606
C     1.200264     -0.010830    -0.722732
C    -1.392913     0.054977    -0.486401
C    -1.393023     0.054742     1.887465
H     1.188447    -0.007400     3.209396
H     3.346414    -0.051385     1.933763
H     3.346507    -0.051838    -0.532317
H     1.188640    -0.008228    -1.808128
O     -1.836703     0.129853    -1.607991
O     -1.836915     0.130622     3.008946
N     -2.152551    -0.029067     0.700486
O     -3.520361     0.118691     0.700416
C     -3.924718     1.462846     0.700575
O     -3.148804     2.375147     0.700901
C     -5.426994     1.508291     0.699955
H     -5.751731     2.548922     0.700886
H     -5.815447     0.994159    -0.184798
H     -5.816335     0.992208     1.583166

H(G3(MP2)-RAD) = -739.863892

PINO nitroxide

C     -0.007493     0.008620    -0.001295
C     -0.007492     0.008601     1.401375
C     1.179497     0.005716     2.123261
C     2.377997     0.002656     1.401129
C     2.377996     0.002619    -0.001053
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<th>Y</th>
<th>Z</th>
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<tr>
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<td>O</td>
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\[ H(G3(MP2)\text{-RAD}) = -586.788696 \]

**PINO_N aminyl radical**

\[
\begin{align*}
| \text{C} & | 0.007550 & 0.006583 & 0.001225 \\
| \text{C} & | 0.007553 & 0.006579 & 1.398855 \\
| \text{C} & | 1.193084 & 0.005653 & 2.126944 \\
| \text{C} & | 2.388401 & 0.004694 & 1.403458 \\
| \text{C} & | 2.388398 & 0.004710 & -0.003381 \\
| \text{C} & | 1.193079 & 0.005679 & -0.726865 \\
| \text{C} & | -1.414869 & 0.007826 & -0.446885 \\
| \text{C} & | -1.414865 & 0.007887 & 1.846971 \\
| \text{H} & | 1.181719 & 0.005689 & 3.212390 \\
| \text{H} & | 3.337122 & 0.003947 & 1.932546 \\
| \text{H} & | 3.337119 & 0.003972 & -0.532471 \\
| \text{H} & | 1.181713 & 0.005720 & -1.812311 \\
| \text{O} & | -1.840440 & 0.008962 & -1.587172 \\
| \text{O} & | -1.840429 & 0.008917 & 2.987259 \\
| \text{N} & | -2.270808 & 0.008259 & 0.700044 \\
\end{align*}
\]

\[ H(G3(MP2)\text{-RAD}) = -511.649841 \]

**PE**
H(G3(MP2)-RAD) = -275.806702

PE_P
H(G3(MP2)-RAD) = -275.14563

PE_S

H(G3(MP2)-RAD) = -275.149628

TBUOH
H(G3(MP2)-RAD) = -233.263565

TBUO
H(G3(MP2)-RAD) = -232.593994

H(G3(MP2)-RAD) = -0.501427
2. Materials

2.1 NAPI Synthesis

*N*-Acetoxyphthalimide (NAPI) was prepared by dissolving *N*-hydroxy-phtalimide NHPI (0.7 g, 4.2 mmol) in 10 mL of acetic anhydride and continuously stirring the mixture for 4 h. The solution was filtered to remove any insoluble NHPI, and the clear filtrate was allowed to cool in the refrigerator, whereupon NAPI precipitated as white crystals. Yield (60 %). $^1$H NMR (δ, CDCl$_3$): 2.4 (CH$_3$, s); 7.8 (2H, d); 7.9 (2H, d). $^{13}$C NMR (δ, CDCl$_3$): 17.6 ; 124, 129, 134.8; 162; 166.6.
2.2 Experimental procedure

**Grafting of TEMPO onto PE in presence of NAPI**

As described above, the grafting reaction of TEMPO onto the LDPE in the molten state was performed in an intermeshing co-rotating twin-screw mini-extruder (ThermoFisher Haake-MiniLab) at 60 rpm and 190°C for 1 hour in presence of NAPI. These experiments were conducted by using two different NAPI/TEMPO molar ratio : 1/4 and 1/6.

**Grafting of Maleic Anhydride onto PE in presence of NAPI and L101**

In a typical process, 5 g of LDPE, MA (4wt% or 2wt%), NAPI (0.5wt%) or L101 (0.4wt%) were added in the preheated mini-extruder simultaneously at a rotor speed of 60 rpm and a temperature of 110°C. After 20 min., the temperature was increased to 230°C and 160°C.
respectively, for 7.5 min. After that, the products were recovered and washed with a purifying solvent such as THF and dried at 120°C under vacuum for 17h to remove the residual MAH.

**Extractions**

Liquid extractions in THF (9 g) in presence of bibenzyle (0.05 wt%, used as reference) were performed at room temperature on 1 g of each film during four days before gas chromatography coupled mass spectrometry analysis.

**Instrumentation**

Gas chromatography-mass spectrometry (GC-MS) was performed with an Agilent 6890 series GC system equipped with a HP-5ms (5%-phenyl)-methylpolysiloxane, ref. 19091S-433. The injector was at 220ºC and the temperature programme followed was: 65-300ºC at 20ºC/min. Injection and detection by MS was carried out at 220ºC.

The FTIR spectra on hot-pressed (250 bars, 160°C) thin films were scan 70 times between ν=4000-400 cm⁻¹ and recorded on a Thermo Nicolet iS10 spectrometer before and after a liquid extraction

Decomposition temperatures were determined through thermogravimetric analysis and recorded on a TGA, DuPont Instruments at a heating rate of 10°C/min.

Liquid ¹H and ¹³C NMR spectra of the resulting polymers were collected in TCE/C6D6 (v/v=2/1) at 90°C with a Brucker Avance III working at 400 MHz.
Rheology testing were performed on a ARES 4800 parallel plate rheometer from TA Instrument. A dynamic frequency sweep test was realized from $\omega=100$ to 0.01 rad/s with a strain of 10 % using specimen disks of 25 mm diameter and 1 mm width molded in hot press. To avoid thermal oxidation of the samples, the heating was provided by a nitrogen flux. Rheology testing allowed us to measure the complex viscosity modulus of the samples at $\omega=1$ rad/s which enable to compare the LDPE microstructure modifications.
3. TGA analyses

TGA of NAPI under oxygen atmosphere.
4. NAPI/PE experiments

Products arising from the reaction involving a mixture of PE and NAPI were analysed by IR, $^1$H NMR and GC-MS.

![IR spectra](image)

**Figure S1:** IR spectra of (a) PEBD heated at 190°C for 1h b)PEBD(5g)+NAPI (1wt%=0.0508g) heated at 190°C for1h (b) before extraction with THF (c) after extraction with THF

One can see a sharp peak at 1720 cm$^{-1}$ corresponding to the stretching of a C=O group signal whose presence may be assigned to oxidation of PE at 190°C (Figure S1a). A similar absorption band at 1720 cm$^{-1}$ is observed for PE after reaction with NAPI (Figures S1b and S1c). Other signals are attributable to NAPI derivatives at around 1746, 1788 et 1809 cm$^{-1}$ (Figure 2b). Upon extracting the adsorbed (non-covalently attached) molecules by extensive washings with THF, the peak at 1809 cm$^{-1}$ disappeared while the bands at 1746, 1788 are maintained (Figure S1c). The latter ones may correspond to grafted NAPI derivatives giving confirmation of hydrogen abstraction onto LDPE. It should be mentioned that a blank
experiment has been done in order to check the efficiency of the NAPI molecules washing procedure by extraction with THF as solvent and we observed that NAPI was completely removed from PE when the reaction media is not heated to 190°C. Indeed, the FTIR spectrum of the mixture PE/NAPI heated to 110°C and extracted with THF does not display any signals in the 1720-1800 cm\(^{-1}\) region (see supporting information, Figure S2).

![Figure S2: IR spectra of (a) PEBD heated at 110°C for 20 min. b)PEBD(5g)+NAPI (1wt%=0.0508g) heated at 110°C for 20 min. (b) before extraction with THF (c) after extraction with THF](image)

GC-MS was carried out on the non-covalently attached molecules removed from the grafted ones by extensive washings with THF in presence of 0.05 wt% of Bibenzyl as reference Three main peaks are observed from 2 min. to 8 min. in the inset of Figure S3.
Figure S3: GC-MS Chromatogramm of products arising from the reaction between PE and NAPI at 190°C; i=impurity coming from solvent.

The peaks located at retention time of 6.4 min. and 5.5 min. can be attributed to NAPI and Phthalimide according to the corresponding mass spectra (Figures S4 and S5, respectively).
Figure S4: Mass spectrum of the peak located at a retention time of 6.4 min. (Figure S3)

Figure S5: Mass spectrum of the peak located at a retention time of 5.2 min. (Figure S3)

The small peaks observed from 8 min. to 14 min. may be attributed to some short PE chains and impurities coming from the solvent. The identification of phthalimide (Figures S3 and S5) in the products arising from the washing procedure of the blend PE/NAPI with THF suggests the hydrogen abstraction ability of NAPI from LDPE. The amount of the NAPI and phthalimide molecules extracted from the washing procedure was calculated from calibration curves based on NAPI and phthalimide in THF-bibenzyl solution (Figure S6 and S7).
Figure S6: Calibration curve of NAPI in THF-Bibenzyle solution

Figure S7: Calibration curve of phthalimide in THF-Bibenzyle solution
The variations of the storage shear modulus versus frequency were then examined for PE and for the blend PE/NAPI (Figure S8) produced at 190°C.

Actually, the variation of the storage modulus is extremely sensitive to a slight modification of the molecular architecture such as branching and crosslinking. In other words, the variation of $G'$ at low frequency (terminal relaxation zone) is a sensitive and a relevant tracer of any modification of chain structure.

![Graph showing variation of storage modulus $G'(\omega)$ versus frequency](image)

**Figure S8:** Variation of the storage modulus $G'(\omega)$ versus frequency determined at 160°C for PE, PE/L101 (1wt%) and PE/NAPI(1wt%) All the samples were processed at 190°C.

From the variation of the storage modulus, Fig S8 shows an extremely slight modification of the PE chain structure in presence of NAPI. Actually the storage modulus is close at low frequency to the storage modulus of PE without any modification of the slope. Unambiguously, the viscoelastic behaviour shows that the chemical modification of the PE in presence of NAPI does not lead to any chain structure modification. Moreover, the $^1$H NMR
spectrum (Figure S9) of the PE/NAPI blend after the washing procedure reveals that a few NAPI-based molecules are grafted onto the PE backbone.

Indeed, the $^1$H NMR spectrum (figure S9) shows signals between 0.5 and 1.7 ppm corresponding to the PE backbone while the acyl group signal of NAPI expected at around 2 ppm has disappeared. The presence of signals at 7.35 ppm and 7.6 ppm corresponding to aromatic protons suggests the grafting of aminyl radicals and/or nitroxyln-based NAPI radicals.

Figure S9: $^1$H NMR spectra of PE/NAPI blend after the washing procedure, solvent TCE/C$_6$D$_6$, T=90°C.
5. NAPI/TEMPO/PE experiments

Figure S10 : Variation of the storage modulus $G'(\omega)$ versus frequency determined at 160°C for PE/NAPI(1wt%) blend produced at 190°C in presence of TEMPO with a NAPI/TEMPO molar ratio of 4 (Δ) and 6 (□)

In the case of functionalized PE, the $^1$H NMR and $^{13}$C NMR were performed in a mixture of trichloroethane and C$_6$D$_6$ at 90°C. The spectra (figure S11) clearly show signals between 0.5 and 2.5 ppm, a broad signal at 3.8 ppm and a small one at 9.6 ppm whatever the TEMPO/NAPI molar ratio. The signals in the range 0.5 and 2.5 ppm can be attributed to the PE backbone while the signal at 3.8 ppm is attributed to grafted TEMPO and in particular to the proton onto the PE backbone in the alpha position with respect to the grafted nitroxide. By comparing the area of signals corresponding to PE (0.5-2.5 ppm) with the area of the signal at 3.8 ppm, the amount of grafted TEMPO was found to be 16% of the initial TEMPO in the
feed whatever the TEMPO/NAPI molar ratio. The signal at 9.6 ppm may be attributed to the formation of an aldehyde function coming from a B-scission reaction onto the PE backbone according to Scheme S1. Indeed, the $^1$H NMR of the product arising from the reaction between NAPI and PE at 190°C after purification also display a signal at 9.6 ppm.

Figure S11: $^1$H NMR spectra of PE grafted TEMPO, solvent TCE/C$_6$D$_6$, T=90°C
a) TEMPO/NAPI molar ratio =4 b) TEMPO/NAPI molar ratio =6
Scheme S1: Reactive pathways of polyethylene based radicals after a thermal homolytic cleavage

Moreover, the $^{13}$C NMR spectrum (Figure S12) exhibits all the signal characteristics of PE and TEMPO.
Figure S12: $^{13}$C NMR spectra of PE grafted TEMPO, solvent TCE/C$_6$D$_6$, T=90°C

a) TEMPO/NAPI molar ratio = 4

As expected, the Cα and Cβ carbon atoms resonate at 33.5 and 26.5 ppm, respectively for the PE part, while Cb and Cc appear at 41 and 60 ppm for the TEMPO one. According to previous studies in this field, the shift of the Ca carbon resonance at 82.5 is indicative of a chemical reaction between TEMPO and PE.

On the basis of these attributions, it is evident that the TEMPO was mainly grafted onto the tertiary carbon atoms of the PE backbone.
6. NAPI/MA/PE experiments

![FTIR spectrum of PE after MA grafting](image)

Figure S13: IR spectra of PEBD(5g)+NAPI (0.5wt%)+MA (4wt%) heated at 110°C for 20 min. and then 230°C for 7.5 min. after extraction with THF

The FTIR spectrum of PE after MA grafting displays carbonyl absorption bands due to the anhydride (1830-1750 cm\(^{-1}\)) and carboxylic acid (1750-1660 cm\(^{-1}\)) and also the absorption band intensity of CH\(_2\) sequences of PE 760-680 cm\(^{-1}\). Then, the MA grafting degree was measured by the aid of a calibration curve using FTIR data (Figure S14) according to the Samay method.
Figure S14: Calibration curve for determination level of MA grafting

$y = 0.4446x$

$R^2 = 0.9929$

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