Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Acyloxyimide Derivatives as Efficient Promoters of Polyolefins C-H Functionalization: Application in the Melt Grafting of Maleic Anhydride onto Polyethylene

Mamy Daniel Rakotonirina,[a, ‡] *Marc Baron,*[b, ‡] *Didier Siri,*[a] *Anouk Gaudel-Siri,*[a] *Sébastien Quinebeche,*[c] *Jean-Jacques Flat,*[c] *Didier Gigmes,*[a] *Philippe Cassagnau,*[b] *Emmanuel Beyou*[b],* *Yohann Guillaneuf*[a,]*

[a] Aix-Marseille Univ., CNRS, ICR UMR 7273, 13397 Marseille, France. E-mail: yohann.guillaneuf@univ-amu.fr ; Fax: +33 (0)4 91 28 87 58; Tel: +33 (0)4 91 28 28 10.

[b] Université de Lyon 1, CNRS, UMR5627 IMP/LMPB, Villeurbanne, France. E-mail: emmanuel.beyou@univ-lyon1.fr

[c] ARKEMA, Centre d'Etude de Recherche et de Développement, 27470, Serquigny, France.

I- General Information

Materials.

All reagents and solvents were purchased from Aldrich or Alfa Aesar and were used as received. Deuterated chloroform ($CDCl_3$) was obtained from Euristop. Thin layer chromatography was performed on precoated silica gel 60-F 254 plates. UV light and phosphomolybdic acid were used for analysis of the TLC plates. Silica gel (40-63 micron) was used for column chromatography.

Characterization

^{1}H, ^{13}C and ^{31}P NMR measurements were performed on both a Bruker Avance DPX 300 MHz spectrometer at 300.13 MHz (^{1}H), 75.47 MHz (^{13}C) and 121.49 MHz (^{31}P) and a Bruker Avance III nanobay 400 MHz spectrometer at 400.13 MHz (^{1}H), 100.61 MHz (^{13}C) and 161.98 MHz (^{31}P) at room temperature in $CDCl_3$ and DMSO-d_6. Tetramethylsilane (TMS) was used as internal standard.

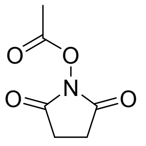
High-resolution MS (HRMS) experiments were performed using a QStar Elite hybrid quadrupole time-of-flight mass spectrometer (Applied Biosystems SCIEX, Concord, ON, Canada) equipped with an electrospray ionization (ESI) source operated in positive mode. The capillary voltage was set at +5500 V and the cone voltage at +75 V. In this hybrid instrument, ions were measured using an orthogonal acceleration time-of-flight (oa-TOF) mass analyzer. Air was used as the nebulizing gas (at a pressure of 10 psi) while nitrogen was used as the curtain gas (at a pressure of 20 psi). Instrument control, data acquisition and data processing of all experiments were achieved using Analyst software (QS 2.0) provided by Applied Biosystems. The polymer sample was dissolved in dichloromethane and further diluted (1:10, v/v) in a methanolic solution of sodium chloride (1 mM). This solution was introduced in the ionization source at a 5 μL.min^{-1} flow rate using a syringe pump. Accurate mass measurements were performed using various sodiated PEG as internal standards.

II- Preparation of acyloxyimides **1-14**

Generally, acetic anhydride or acyl chlorides were added to hydroxyimide derivatives in bulk or in solution using dry dichloromethane (CH_2Cl_2) or dry tetrahydrofuran (THF). When using acyl chloride, triethylamine (Et_3N) was introduced dropwise under inert atmosphere (argon or nitrogen). The mixture was stirred at room temperature.

1. Synthesis of succinimide derivatives (NAS - 1, tBu-NAS - 2, Ph-NAS - 3, DiA-NAS - 4, DSO - 5)

2,5-dioxopyrrolidin-1-yl acetate **(NAS - 1)**

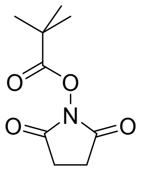


In a typical procedure, acetic anhydride (5 mL, d= 1.08, n= 52.90 mmol, MM= 102.09 g.mol^{-1}) was added to hydroxysuccinimide (2.00 g, n= 17.38 mmol, MM= 115.09 g.mol^{-1}) and stirred at room temperature (25°C) for 4 hours under air. The formed precipitate was collected by filtration and washed with cold pentane yielding the pure product as a white solid (2.09 g, 13.31 mmol, 80 % yield).

^{1}H NMR ($CDCl_3$, 300MHz) δ(ppm): 2.84 (s, 4H), 2.34 (s, 3H)[5]; ***^{13}C NMR ($CDCl_3$, 400MHz) δ(ppm):*** 169.02 (Cq, OCO) 165.56 (2 x Cq, **C**=O), 25.56 (2 x **C**H_2, imide), 17.51 (**C**H_3); ***Mp:*** 125.3-127.9 °C.

HRMS m/z: theor: 180.0027 found: 180.0266 ([M+Na]$^+$ detected).

2,5-dioxopyrrolidin-1-yl pivalate **(tBu-NAS - 2)**

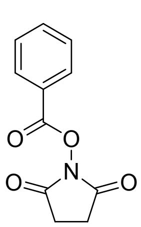


To a solution of hydroxysuccinimide (5g, n= 43.45 mmol, MM= 115.09 g.mol^{-1}) in 50 mL dichloromethane, triethylamine (6.06 mL, d= 0.726, n= 43.45 mmol, 1 equiv, MM= 185.35 g.mol^{-1}) and pivaloyl chloride (5.35 mL, d= 0.979, n= 43.45 mmol, 1 equiv, MM= 120.58 g.mol^{-1}) were introduced dropwise at room temperature. The reaction mixture was stirred overnight under argon. The obtained cloudy solution was then filtered and the corresponding recovered solution was washed by 3 x 50 mL water (extraction of amine and ammonium salts). Then, the combined organic phases were dried over $MgSO_4$ and filtered. The solvent was removed under vacuum, giving the pure product as a white solid (6.51 g, 32.68 mmol, 75 % yield).

^{1}H NMR ($CDCl_3$, 300MHz) δ(ppm): 2.83 (s, 4H), 1.39 (s, 9H); ***^{13}C NMR ($CDCl_3$, 400MHz) δ(ppm):*** 173.39 (Cq, O**C**O) 162.12 (2 x Cq, **C**=O), 38.36 (Cq, alkyl), 26.95 (2 x **C**H_2, imide) 25.62 (3 x **C**H_3); ***Mp:*** 56.1 – 58.7 °C.

HRMS m/z: theor: 222.0737 found: 222.02732 ($[M+Na]^+$ detected).

2,5-dioxopyrrolidin-1-yl benzoate (Ph-NAS - 3)

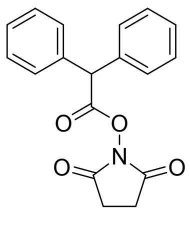


To a solution of hydroxysuccinimide (3.00 g, n= 26.07 mmol, MM= 115.09 g.mol^{-1}) in 20 mL dichloromethane, triethylamine (3.63 mL, d= 0.726, n= 26.07 mmol, 1 equiv, MM= 101.19 g.mol^{-1}) and benzoyl chloride (3.03 mL, d= 1.21, n= 26.07 mmol, 1 equiv, MM= 140.57 g.mol^{-1}) were added dropwise and stirred at room temperature for 20h hours under argon. The reaction mixture was then washed by 3 x 30 mL water and the combined organic phases were dried over $MgSO_4$ and were filtered. The solvent was removed under vacuum, yielding the pure product (5.33 g, 24.07 mmol, 92 % yield).

^{1}H NMR ($CDCl_3$, 300MHz) δ(ppm): 8.15 (d, 2H, ^{3}J= 7.70Hz) 7.67-7.72 (t, 1H, ^{3}J= 7.52Hz), 7.50-7.55 (m, 2H), 2.91 (s, 4H); ***^{13}C NMR ($CDCl_3$, 400MHz) δ(ppm):*** 169.15 (Cq, O**C**O) 162.04 (2 x Cq, **C**=O), 134.87 (**C**H, Bz) 130.57 (2 x **C**H, Bz), 128.84 (2 x **C**H, Bz) 99.99 (**C**q, Bz), 25.68 (2 x **C**H_2, imide); ***Mp:*** 132.1 - 133.9 °C.[6]

HRMS m/z: theor: 242.0424 found: 242.0417 ($[M+Na]^+$ detected).

2,5-dioxopyrrolidin-1-yl diphenylacetate (DiA-NAS - 4)

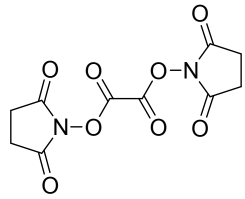


To a solution of succinimide (2.00 g, n= 17.18 mmol, MM= 115.09 g.mol^{-1}) in 20 mL dichloromethane, triethylamine (2.42 mL, d= 0.726, n= 17.38 mmol, 1 equiv, MM= 101.19 g.mol^{-1}) and diphenylacetyl chloride (4.01 g, n= 17.38 mmol, 1 equiv, MM= 230.69 g.mol^{-1}) were added dropwise and stirred at room temperature overnight.. The obtained colored solution was then washed by 3 x 40 mL water and the combined organic phases were dried over $MgSO_4$

and filtered. After removing the solvent under vacuum, the obtained solid compound was washed with 2 x 30 mL of diethyl ether and filtrated to afford a white powder (4.00 g, 11.67 mmol, 67 % yield).

^{1}H NMR (DMSO$_6$, 300MHz) δ(ppm): 7.81-7.28 (m, 10H), 5.75 (s, 1H), 2.82 (s, 4H); ***HRMS (ESI MS) m/z:*** theor: 327.1339 found: 327.1341 ([M+NH4]$^+$ detected); ***Mp:*** 109.9 - 112 °C.

bis(2,5-dioxopyrrolidin-1-yl) oxalate (DSO - 5)

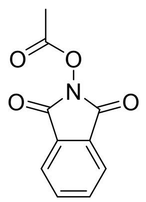


To a solution of hydroxyphthalimide (1.00 g, n= 8.69 mmol, MM= 115.09 g.mol^{-1}) in 20 mL acetonitrile, triethylamine (1.21 mL, d= 0.726, n= 8.69 mmol, 2 equiv, MM= 101.19 g.mol^{-1}) and oxalyl chloride (0.373 mL, d= 1.48, n= 4.34 mmol, 0.5 equiv, MM= 126.93 g.mol^{-1}) were added dropwise at 0°C and the reaction mixture was then stirred for 3 hours under argon at room temperature (25°C). The obtained cloudy solution was diluted with water and the formed precipitate was recovered by filtration and washed with 2 x 10 mL of water and then with 2 x 10 mL of THF. Finally, a white solid was obtained after a drying procedure under vacuum (1.13 g, 3.98 mmol, 91 % yield).

^{1}H NMR (DMSO-d$_6$, 300MHz) δ(ppm): 2.59 (s, 8H); ***^{13}C NMR (DMSO-d$_6$, 400MHz) δ(ppm):*** 172.71 (Cq, O**C**O) 160.90 (4 x Cq, **C**=O), 25.21 (4 x **C**H$_2$, imide); ***HRMS m/z:*** theor: 307.0173 found: 307.017 ([M+Na]$^+$ detected).

2. Synthesis of phthalimide derivatives

1,3 dioxoisoindolin-2-yl acetate **(NAPI - 6)**

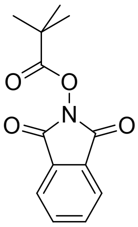


Acetic anhydride (30 mL, d= 1.08, n= 317.37 mmol, MM= 102.09 g.mol^{-1}) was added to hydroxyphthalimide (10.06 g, n= 61.67 mmol, MM= 163.13 g.mol^{-1}) at room temperature (25°C) and the reaction mixture was stirred for 4 hours under air. The obtained precipitate was collected by filtration and washed with cold pentane to afford the pure product as white crystals (11.83 g, 53.62 mmol, 94 % yield).

^{1}H NMR ($CDCl_3$, 300MHz) δ(ppm): 7.93-7.76 (dm, 4H), 2.4 (s, 3H); ***^{13}C NMR ($CDCl_3$, 300MHz) δ(ppm):*** 166.52 (Cq, OCO) 161.87 (2 x Cq, **C**=O), 134.75 (2 x **C**H, imide), 128.90 (2 x Cq, imide) 123.98 (2x **C**H, imide), 17.60 (**C**H_3);[1] ***Mp:*** 185.6-188.2 °C.

HRMS m/z: theor: 228.0267 found: 228.0262 ($[M+Na]^+$ detected).

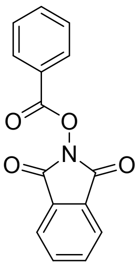
1,3 dioxoisoindolin-2-yl pivalate (tBu-NAP - 7)



To a solution of hydroxyphthalimide (10.00 g, n= 61.30 mmol, MM= 163.13 g.mol^{-1}) in 60 mL dichloromethane, tributylamine (14.60 mL, d= 0.778, n= 61.30 mmol, 1 equiv, MM= 185.35 g.mol^{-1}) and pivaloyl chloride (7.55 mL, d= 0.979, n= 61.30 mmol, 1 equiv, MM= 120.58 g.mol^{-1}) were added dropwise stirred for 18h hours under argon at room temperatures. The corresponding yellow solution was then washed by 3 x 50 mL water and the combined organic phases were dried over $MgSO_4$ and filtered. After removing the solvent under vacuum, a white solid was obtained (11.18 g, 247.25 mmol, 71 % yield).

^{1}H NMR ($CDCl_3$, 300MHz) δ(ppm): 7.92-7.76 (dm, 4H), 1.44 (s, 9H); ***^{13}C NMR ($CDCl_3$, 400MHz) δ(ppm):*** 174.36 (Cq, OCO) 162.08 (Cq, **C**=O), 134.62 (**C**H, imide), 129.12 (Cq, imide) 123.84 (**C**H, imide, 38.41 (Cq, alkyl), 27.03 (**C**H_3);[7] ***Mp:*** 59.4 – 62.2 °C.
HRMS m/z: theor: 270.0737 found: 270.0736 ($[M+Na]^+$ detected).

1,3 dioxoisoindolin-2-yl benzoate (Ph-NAP - 8)

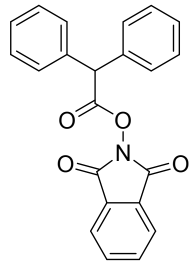


To a solution of hydroxyphthalimide (1.00 g, n= 6.13 mmol, MM= 163.13 g.mol^{-1}) in 20 mL dichloromethane, triethylamine (1.07 mL, d= 0.726, n= 7.61 mmol, 1.25 equiv, MM= 101.19 g.mol^{-1}) and benzoyl chloride (0.712 mL, d= 1.21, n= 6.13 mmol, 1 equiv, MM= 140.57 g.mol^{-1}) were added dropwise at room temperature and the reaction mixture was stirred for 20h hours under argon. The obtained colored solution was then washed by 3 x 50 mL and the combined organic phase were dried over $MgSO_4$ and filtered. The solvent was then removed under vacuum yielding the pure product as a beige solid (1.48 g, 5.55 mmol, 90 % yield).

^1H NMR ($CDCl_3$, 300MHz) δ(ppm): 8.21 (d, 2H, ^3J= 15Hz), 7.92-7.79 (dm, 4H), 7.71 (t, 1H, ^3J= 7.52Hz), 7.55 (t, 2H, ^3J= 7.70Hz); ***^{13}C NMR ($CDCl_3$, 400MHz) δ(ppm):*** 162.77 (Cq, OCO) 161.99 (2 x Cq, **C**=O), 134.82 (**C**H, Bz), 134.74 (2 x Cq, imide) 130.57 (2 x **C**H, Bz), 129.01 (2 x Cq, imide), 128.83 (2 x **C**H, Bz), 125.31 (Cq, Bz), 123.94 (CH, imide);[7] ***Mp:*** 162.6 - 164.8 °C.

HRMS m/z: theor: 290.0424 found: 290.0421 ($[M+Na]^+$ detected).

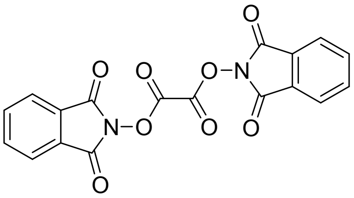
1,3 dioxoisoindolin-2-yl diphenylacetate (DiA-NAP - 9)



To a solution of hydroxyphthalimide (2.15 g, n= 13.18 mmol, MM= 163.13 g.mol^{-1}) in 20 mL dichloromethane, triethylamine (1.84 mL, d= 0.726, n= 13.18 mmol, 1 equiv, MM= 101.19 g.mol^{-1}) and diphenylacetyl chloride (3.04 g, n= 13.18 mmol, 1 equiv, MM= 230.69 g.mol^{-1}) were added dropwise and the reaction mixture was stirred overnight under argon. The obtained colored solution was then washed by 3 x 40 mL water and the combined organic phase were dried over $MgSO_4$ and filtered. Then, the solvent was removed under vacuum and the obtained solid compound was washed with 2 x 30 mL of diethyl ether and recovered by filtration as a white powder (2.99 g, 8.37 mmol, 64 % yield).

^1H NMR ($CDCl_3$, 300MHz) δ(ppm): 7.99-7.93 (dm, 4H), 7.45-7.3 (m, 10H), 5.86 (s, 1H); ***HRMS (ESI MS) m/z:*** theor: 375.1339 found: 375.1336 ($[M+NH4]^+$ detected); ***Mp:*** 146.1 - 148.3 °C.

bis(1,3 dioxoisoindolin-2-yl) oxalate (DPO - 10)

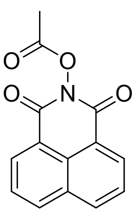


To a solution of hydroxyphthalimide (2.00 g, n= 12.26 mmol, MM= 163.13 g.mol^{-1}) in 25 mL tetrahydrofuran, w triethylamine (1.71 mL, d= 0.726, n= 12.26 mmol, 1 equiv, MM= 101.19 g.mol^{-1}) and oxalyl chloride (0.525 mL, d= 1.48, n= 6.13 mmol, 0.5 equiv, MM= 126.93 g.mol^{-1}) were added dropwise at 0°C. Then, the reaction mixture was stirred for 3 hours under argon at room temperature (25°C). The cloudy solution was diluted in water. The obtained precipitate was then filtered and washed with 2 x 20 mL of water and then with 2 x 20 mL of THF. The recovered product was dried under vacuum yielding a white solid (1.65 g, 4.34 mmol, 70 % yield).

^{1}H NMR (DMSO-d_6, 300MHz) δ(ppm): 7.83 (s, 8H); ***^{13}C NMR (DMSO-d_6, 400MHz) δ(ppm):*** 164.11 (Cq, O**C**O) 164.02 (2 x Cq, **C**=O), 134.52 (2 x **C**H, imide) 128.75 (2 x Cq, imide), 122.96 (2 x **C**H, imide); ***HRMS (ESI MS) m/z:*** theor: 398.0619 found: 398.0620 ([M+NH4]$^+$ detected).

3. Synthesis of naphthalimide derivatives

1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl acetate (NANPI - 11)

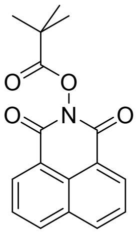


Acetic anhydride (40 mL, d= 1.08, n= 423.16 mmol, MM= 102.09 g.mol^{-1}) was added to hydroxynaphthalimide sodium salt (8.29 g, n= 35.25 mmol, MM= 235.17 g.mol^{-1}) at room temperature (25°C) and the reaction was stirred for 4 hours under air. The obtained precipitate was collected by filtration and washed with water to afford the pure product as a beige solid (8.93 g, 33.95 mmol, 96 % yield).

^{1}H NMR (CDCl$_3$, 300MHz) δ(ppm): 8.62-8.64 (d, 2H), 8.29-8.26 (d, 2H), 7.82-7.76 (t, 2H), 2.48 (s, 3H); ***^{13}C NMR (CDCl$_3$, 300MHz) δ(ppm):*** 166.62 (Cq, O**C**O) 159.52 (2 x Cq, **C**=O), 134.97 (2 x **C**H, imide), 131.88 (2 x **C**H, imide), 127.63 (2 x Cq, imide), 127.08 (2x **C**H, imide), 122.33 (Cq, imide), 17.83 (**C**H$_3$).

HRMS m/z: theor: 278.0424 found: 278.0425 ([M+Na]$^+$ detected).

1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl pivalate (tBu-NANP - 12)

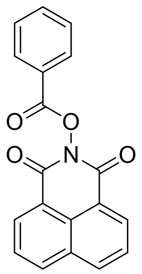


To a solution of hydroxynaphthalimide sodium salt (10.00 g, n= 42.52 mmol, MM= 235.17 g.mol^{-1}) in 80 mL dichloromethane, pivaloyl chloride (5.24 mL, d= 0.979, n= 42.52 mmol, 1 equiv, MM= 120.58 g.mol^{-1}) was added at room temperature and the reaction mixture was stirred overnight under argon. The obtained colored solution was washed by 3 x 50 mL water and the combined organic phases were dried over $MgSO_4$ and filtered. After removing the solvent under vacuum, a beige powder was obtained (10.52 g, 32.91 mmol, 77 % yield).

^1H NMR ($CDCl_3$, 300MHz) δ(ppm): 8.61 (d, 2H), 8.26 (d, 2H), 7.78 (t, 2H), 1.52 (s, 9H); ***^{13}C NMR ($CDCl_3$, 400MHz) δ(ppm):*** 174.18 (Cq, OCO) 159.62 (2 x Cq, **C**=O), 134.85 (2 x **C**H, imide), 131.89 (2 x **C**H, imide), 127.64 (2 x Cq, imide), 127.07 (2x **C**H, imide), 122.49 (Cq, imide), 38.59 (Cq, alkyl) 27.11 (3 x **C**H_3). ***Mp:*** 167.2 – 169.9 °C.

HRMS m/z: theor: 320. 0893 found: 320.0892 ($[M+Na]^+$ detected).

1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl benzoate (Ph-NANP - 13)

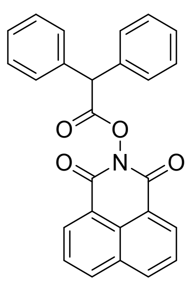


To a solution of hydroxynaphthalimide sodium salt (10.08 g, n= 42.86 mmol, MM= 235.17 g.mol^{-1}) in 20 mL dichloromethane, benzoyl chloride (4.98 mL, d= 1.21, n= 42.86 mmol, 1 equiv, MM= 140.57 g.mol^{-1}) was added dropwise and the reaction mixture was stirred for 20h hours under argon. Then, the obtained yellow solution was washed with 3 x 50 mL water and the combined organic phases were dried over $MgSO_4$ and filtered. After removing the solvent under vacuum, a yellow solid was obtained (10.71 g, 32.07 mmol, 75 % yield).

^1H NMR ($CDCl_3$, 300MHz) δ(ppm): 8.66 (d, 2H), 8.28 (m, 4H), 7.81 (t, 2H), 7.71 (t, 1H) 7.56 (t, 2H); ***Mp:*** 264.3 - 266 °C.

HRMS m/z: theor: 340.0580 found: 340.0579 ($[M+Na]^+$ detected).

1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl diphenylacetate (DiA-NANP - 14)



To a solution of hydroxynaphthalimide sodium salt (1.00 g, n= 4.25 mmol, MM= 235.17 g.mol^{-1}) in 15 mL dichloromethane, diphenylacetyl chloride (0.98 g, n= 4.25 mmol, 1 equiv, MM= 230.69 g.mol^{-1}) was added and the reaction mixture was stirred overnight under argon. The obtained colored solution was washed with 3 x 40 mL of water and the combined organic phases were dried over $MgSO_4$ and filtered. The solvent was removed under vacuum and the obtained solid compound was washed with 2 x 30 mL of diethyl ether and then isolated by filtration yielding a white powder (1.21 g, 2.97 mmol, 70 % yield).

^{1}H NMR ($CDCl_3$, 300MHz) δ(ppm): 8.63-8.6 (d, 2H), 8.27-8.24 (d, 2H), 7.77 (t, 2H), 7.53-7.34 (m, 10H), 5.55 (s, 1H); ***^{13}C NMR ($CDCl_3$, 400MHz) δ(ppm):*** 168.87 (Cq, O**C**O), 159.44 (2 x Cq, **C**=O), 137.20 (2 x Cq, alkyl), 134.96 (2 x **C**H, imide), 131.94 (2 x **C**H, imide) 131.89 (2 x **C**q, imide), 128.94 (2 x **C**H, alkyl), 128.76 (4 x **C**H, alkyl) 127.73 (4 x CH, alkyl) 127.64 (2 x Cq, imide), 127.07 (2x **C**H, imide), 122.49 (Cq, imide), 54.50 (**C**H, alkyl); ***HRMS (ESI MS) m/z:*** theor: 425.1496 found: 425.1497 ($[M+NH4]^+$ detected); ***Mp:*** 181.3 - 183 °C.

III- Determination of the MA grafting by FT-IR

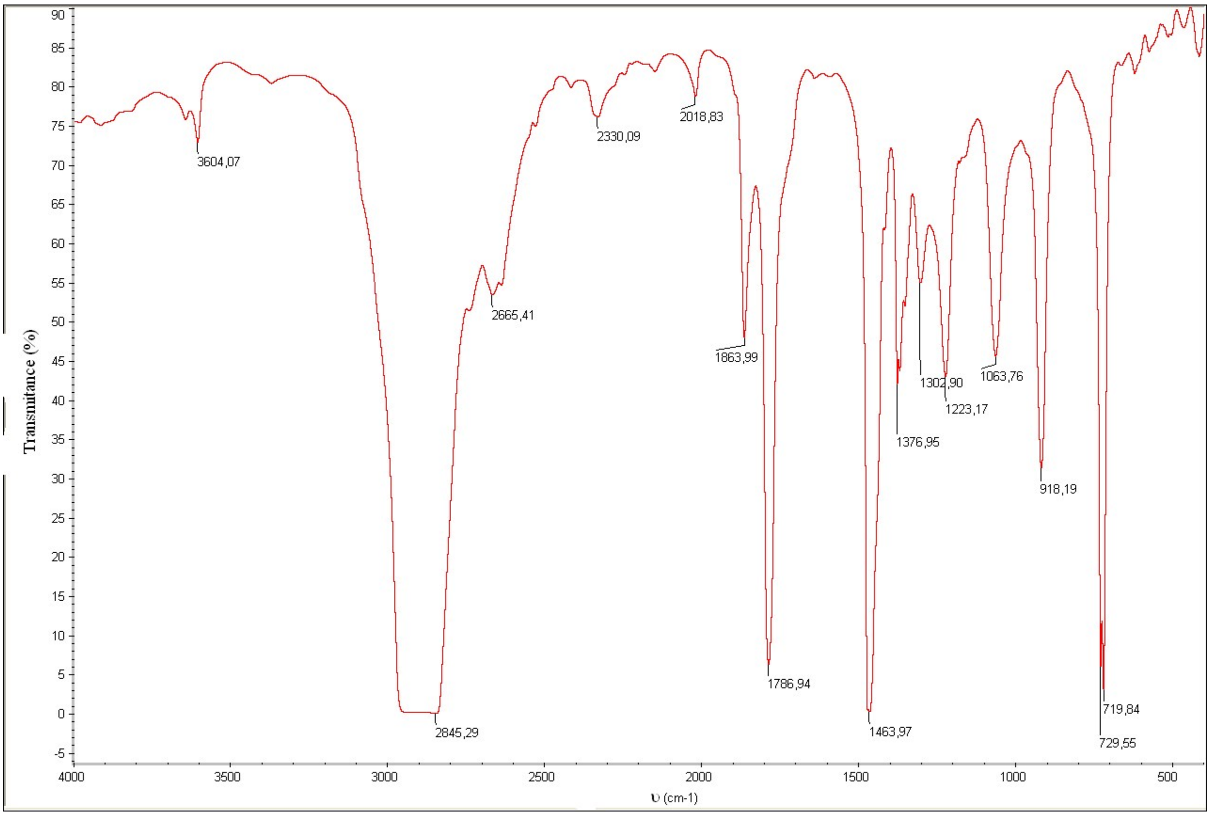


Fig. S1. IR spectra of PEBD(5g)+NAPI (0.5wt%)+MA (4wt%) heated at 110°C for 20 min. and then 230°C for 7.5 min. after extraction with THF.

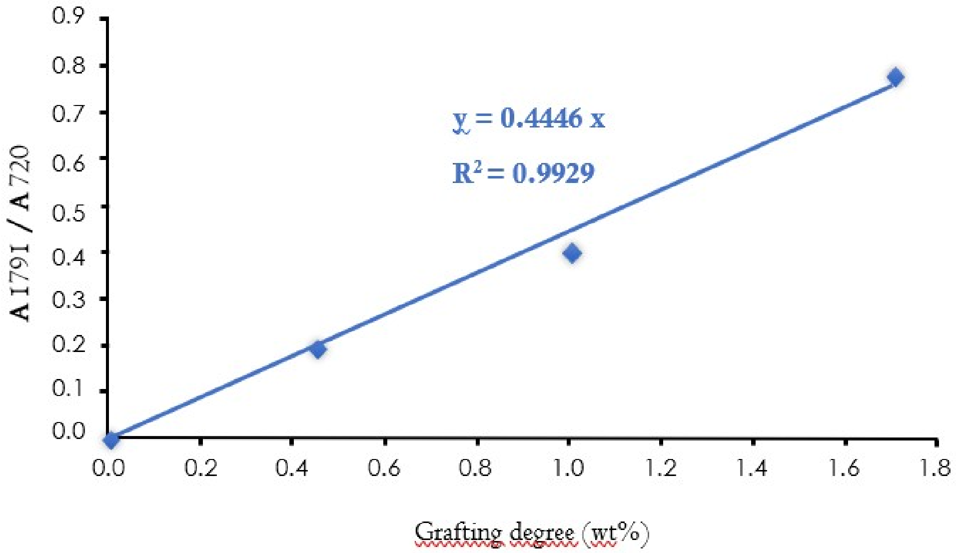


Fig. S2. Calibration curve for determination level of MA grafting.