Polyamide precursors from renewable 10-undecenenitrile and methyl acrylate via olefin cross-metathesis

X. Miao,[a] C. Fischmeister,[a] P. H. Dixneuf,[a] C. Bruneau,[a] J.-L. Dubois,[b] J.-L. Couturier[c]

[a]UMR 6226-CNRS –Université de Rennes 1, Institut des Sciences Chimiques de Rennes, Campus de Beaulieu, 35042, Rennes cedex, France.
[b]Arkema, , 420 Rue d'Estienne d'Orves, 92705 Colombes (France)
[c]Arkema, CRRA, BP 63, rue Henry Moissan, 69493, Pierre Bénite (France)

Supporting Information

General Informations

All reactions were carried out with exclusion of air using Schlenk tube techniques. Organic solvents were dried by standard procedures and distilled under argon prior to use. 10-Undecenitrile supplied by Arkema was distilled under vacuum and stored under Argon prior to use. Methyl acrylate was purchased from Acros Organics and stored under Argon over 4 A MS prior to use. *t*BuOK (98%) was purchased from Alfa Aesar and stored under Argon. ^{1}H NMR spectra were recorded at 200 MHz and 300 MHz. ^{13}C NMR spectra were recorded at 50.3 MHz and 75.5 MHz. Reactions were monitored using a Shimadzu 2014 gas chromatograph equipped with Equity $^{\text{TM}}$ – 1 Fused Silica capillary column. Pure products were obtained by column chromatography on silica gel (Merck Silica Gel 60) using mixtures of petroleum ether and diethyl ether or a mixture of petroleum ether and ethyl acetate as the eluent. High resolution mass spectrometry data (HR-MS) was recorded using Varian Mat 311 equipped with a magnetic field, an electric field (geometry BE) and a room of collisions. Elemental analysis data were obtained on a microanalysor (Microanalyseur Flash EA1112 CHNS/O Thermo Electron). Products were further analyzed by GC-MS on a Shimadzu QP2010S apparatus.

General procedure for the cross-metathesis of 10-undecenitrile 1 with methyl acrylate.

83 mg of **1** (0.5 mmol, 1 equiv.) and 0.09 ml of methyl acrylate (1 mmol, 2 equiv.) were dissolved in 10 ml of distilled toluene with dodecane (10 µl) as internal standard. 1.6 mg of complex **II** (0.5 mol%) was added and the reaction was stirred at 50 °C for 1 h. After solvent evaporation, the product was purified by column chromatography on silica gel using a mixture of petroleum ether/diethyl ether (8/2) as eluent to furnish **3** as a mixture of *E* and *Z* isomers that could be partially separated during column chromatography purification.

E isomer:

^{1}H NMR (300.13 MHz, $CDCl_3$) δ ppm: 1.32-1.71 (m, 12 H, 6 C<u>H</u>$_2$); 2.20 (m, 2 H, C<u>H</u>$_2$CH=CHCO); 2.34 (t, 2 H, $^3J_{HH}$ = 7.0 Hz, NCC<u>H</u>$_2$); 3.73 (s, 3 H, OC<u>H</u>$_3$); 5.83 (d, 1 H, $^3J_{HH}$ = 15.7 Hz, CH=C<u>H</u>CO); 6.70 (dt, 1 H, $^3J_{HH}$ = 15.7 Hz, $^3J_{HH}$ = 7.0 Hz, C<u>H</u>=CHCO).

^{13}C NMR (75.5 MHz, $CDCl_3$) δ ppm: 17.1, 25.3, 27.9, 28.6, 28.6, 28.9, 29.0, 32.1 (<u>C</u>H$_2$); 51.4 (O<u>C</u>H$_3$); 119.8 (<u>C</u>N); 120.9 (CH=<u>C</u>HCO$_2$Me); 149.6 (<u>C</u>H=CHCO$_2$Me); 167.2 (<u>C</u>=O).

Elemental Analysis: Calculated for $C_{13}H_{21}NO_2$: C: 69.92; H: 9.48; N: 6.27; found: C: 69.27; H: 9.45; N: 6.42

HRMS: $[M+Na]^+$ ($C_{13}H_{21}NO_2Na$) m/z Calculated : 246.1470, measured: 246.1469

Z isomer

^{1}H NMR (300.13 MHz, $CDCl_3$) δ ppm: 1.34-1.72 (m, 12 H, 6 C<u>H</u>$_2$); 2.35 (t, 2 H, $^3J_{HH}$ = 7.1 Hz, NCC<u>H</u>$_2$); 2.66 (m, 2 H, C<u>H</u>$_2$CH=CHCO); 3.72 (s, 3 H, OC<u>H</u>$_3$); 5.79 (dt, 1 H, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 1.5 Hz, CH=C<u>H</u>CO); 6.70 (dt, 1 H, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 7.5 Hz, C<u>H</u>=CHCO).

General procedure for the cross-metathesis of 10-undecenitrile 1 with methyl acrylate using syringe pump slow addition of catalyst.

332 mg of **1** (2 mmol, 1 equiv.) and 0.36 ml of methyl acrylate (4 mmol, 2 equiv.) were dissolved in 38 ml of distilled toluene with dodecane (10 µl) as internal standard. The desired amount of catalyst was dissolved in 2 ml of toluene and added dropwise over a period of 2 h 40 min into the reaction mixture heated at the desired temperature (see picture). After completion of the catalyst addition, the reaction was stirred for 2 h 20 min. Total reaction time 5 h.

Representative general Procedure for Tandem Cross-metathesis of 1 with methyl acrylate / Hydrogenation to saturated amino-ester 7

83 mg of **1** (0.5 mmol, 1 equiv.) and 0.09 ml of methyl acrylate (1 mmol, 2 equiv.) were dissolved in 10 ml of distilled toluene with dodecane (10 µl) as internal standard. 9.4 mg (0.015 mmol, 3 mol%) of complex **II** were added and the reaction mixture stirred at room temeperature for 1h. The crude reaction solution containing the residual ruthenium was transferred into an autoclave. ^{t}BuOK (0.15 mmol, 16.8 mg, 30 mol%)) was added and the reactor was pressurised with 20 bar of H_2. The reaction was stirred at 80 °C for 40 h. After solvent evaporation the product was purified by extraction dichloromethane / 1 N HCl and dichloromethane / 1 N NaOH to furnish **7** as a yellowish solid. M = 102 mg (yield = 90%).

^{1}H NMR (300.13 MHz, CD_3OD) δ ppm: 1.33 (broad s, 14 H, 7 $C\underline{H}_2$); 1.54-1.64 (m, 4 H, $C\underline{H}_2CH_2NH_2$ + $C\underline{H}_2CH_2CO_2Me$); 2.33 (t, 2 H, $^3\boldsymbol{J}_{HH}$ = 7.4 Hz, $C\underline{H}_2CO_2Me$); 2.76 (t, 2 H, $^3\boldsymbol{J}_{HH}$ = 7.4 Hz, $C\underline{H}_2NH_2$); 3.66 (s, 3 H, $OC\underline{H}_3$).

^{13}C NMR (75.5 MHz, CD_3OD) δ ppm: 24.7, 26.7, 28.9, 29.1, 29.3, 29.4, 29.4, 29.6, 32.1, 33.5, 41.1 ($\underline{C}H_2$); 50.6 ($O\underline{C}H_3$); 174.2 ($\underline{C}$=O).

HRMS: $[M+H]^+$ ($C_{13}H_{28}NO_2$) m/z calculated: 230.2120, measured: 230.2121
$[M+Na]^+$ ($C_{13}H_{27}NO_2Na$) m/z calculated: 252.1939, measured: 252.1937