Electronic Supplementary Material (ESI) for Polymer Chemistry

New Efficient Delayed-Action Catalysts Based on Guanidine Templates for Polyurethane Synthesis

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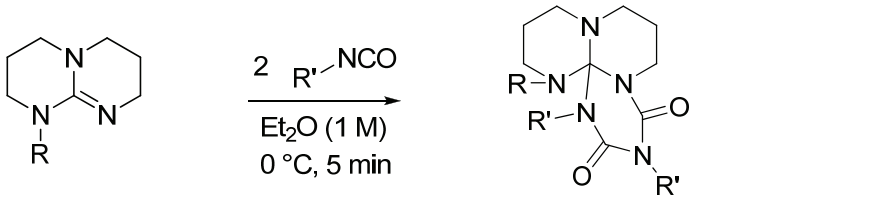
• General information

All reactions were carried out under argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Yields refer to chromatographically and spectroscopically (^{1}H and ^{13}C NMR) homogeneous materials, unless otherwise stated. Commercial reagents were used without further purification, unless otherwise stated. ^{1}H NMR and ^{13}C NMR were recorded on a Brüker AC-300 FT and (^{1}H: 300 MHz, ^{13}C: 75.46 MHz) and a Brüker ARX-400 FT (^{1}H: 400 MHz, ^{13}C: 100.6 MHz) using $CDCl_3$ as internal reference unless otherwise indicated. The chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz respectively. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet, br = broad. IR spectra were recorded on a Perkin-Elmer 1710 spectrophotometer, on a Perkin-Elmer Paragon 500 FT-IR spectrophotometer or on a Perkin-Elmer Mattson Unicam 500 16PC FT-IR using a ZnSe crystal ATR accessory. High resolution mass spectra (HRMS) were recorded with a Q-TOF 2 spectrometer in the electrospray ionisation (ESI) mode. Melting points were not corrected and determined by using a Büchi Totolli apparatus. Merk silica gel 60 (70-230 mesh) was used for flash chromatography. Size exclusion chromatography (SEC) analyses were performed at room temperature in DMF at 80°C with a setup consisting of a PL-GPC 50 plus Integrated GPC from Polymer laboratories-Varian and a series of three columns PLgel 5µm MIXED-D. The elution of the filtered samples was monitored using simultaneous UV and refractive index detections. The elution times were converted to molar mass using a calibration curve based on low dispersity (M_w/M_n) polystyrene (PS) standards.

- **General procedure for the synthesis of guanidine derivatives 2a-c**

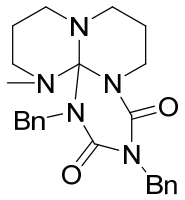


1a, R = Me
1b, R = Bn

R, R' = Me, CycCH$_2$: **2b**, 81 %
R, R' = Me, Bn: **2a**, 89 %
R, R' = Bn, Bn : **2c**, 67 %

Benzylisocyanate (2 mmol) was added dropwise to a solution of guanidine (1 mmol) in Et_2O (1 mL) at 0 °C. The homogeneous reaction mixture was stirred 5 min at 0°C. After recrystallization of the crude mixture at –40 °C, the crystals were filtered and washed with a small amount of ether affording the expected heterocycle as a colorless solid.

➢ MTBD-2 BnNCO adduct **2a**



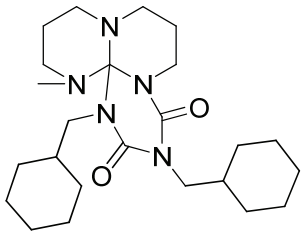
Chemical Formula: $C_{24}H_{29}N_5O_2$
Molecular Weight: 419,52

Following the general procedure above, a mixture of MTBD **1a** (150 µL, 1.04 mmol) and benzylisocyanate (256 µL, 2.09 mmol) provided after crystallization the expected guanidine adduct **2a** as a colorless solid (389 mg, 89 %).

Monocrystals were grown by slow evaporation of a THF solution of **2a** at room temperature for XRD structure determination.

Mp = 96-97 °C (THF/ pentane); IR (neat): ν = 2925, 1683, 1645, 1470, 1377, 751, 700 cm^{-1}; ^{1}H NMR (C_6D_6, 300 MHz): δ = 7.79 – 7.73 (m, 2H), 7.56 – 7.50 (m, 2H), 7.25 – 7.01 (m, 6H), 5.31 (dd, J = 11.7 Hz, J = 13.7 Hz, 2H), 5.06 (d, J = 14.1 Hz, 1H), 4.63 – 4.52 (m, 1H), 4.35 (d, J = 14.1 Hz, 1H), 2.55 – 2.42 (m, 2H), 2.30 – 2.08 (m, 4H), 1.79 (s, 3H), 1.72 – 1.47 (m, 2H), 1.25 – 1.08 ppm (m, 3H), ^{13}C NMR (C_6D_6, 75 MHz): δ = 153.7, 151.4, 140.5, 139.1, 130.0, 129.4, 128.5, 127.5, 126.9, 97.3, 47.8, 46.8, 45.7, 45.1, 42.2, 36.4, 35.7, 23.3, 20.5 ppm; HRMS (ESI): m/z calcd for $C_{24}H_{30}N_5O_2$ $[M+H]^+$: 420.23995, found: 420.2396.

➢ MTBD-2 CycCH_2NCO adduct **2b**



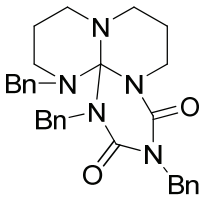
Chemical Formula: $C_{24}H_{41}N_5O_2$
Molecular Weight: 431,61

Following the general procedure above, a mixture of MTBD **1a** (150 µL, 1.04 mmol) and cyclohexanemethyl isocyanate (284 µL, 1.98 mmol) provided after crystallization the expected guanidine adduct **2b** as a colorless solid (347 mg, 81 %).

Monocrystals were grown by slow evaporation of a THF solution of **2b** at room temperature for XRD structure determination.

Mp = 115-118 °C (Et_2O); IR (neat): ν = 2922, 2848, 1692, 1649, 1445, 1274 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ = 4.69 (ddd, J = 13.9, 8.7, 1.3 Hz, 1H), 4.10 (qd, J = 13.0, 6.9 Hz, 2H), 3.66 (dd, J = 13.1, 6.6 Hz, 1H), 3.20 (dd, J = 13.1, 6.7 Hz, 1H), 2.75 – 2.59 (m, 3H), 2.42 – 2.27 (m, 3H), 2.12 – 2.01 (m, 2H), 2.07 (s, 3H), 2.00 – 1.06 ppm (m, 26 H), ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 154.1, 151.9, 97.8, 49.6, 48.5, 47.8, 46.1, 43.0, 38.2, 37.9, 36.5, 35.6, 31.9, 31.6, 31.4, 27.0, 26.9, 26.6, 26.5, 26.4, 23.5, 21.8 ppm; HRMS (ESI): m/z calcd for $C_{24}H_{42}N_5O_2$ $[M+H]^+$: 432.33385, found: 432.3339.

➢ BnTBD-2 BnNCO adduct **2c**



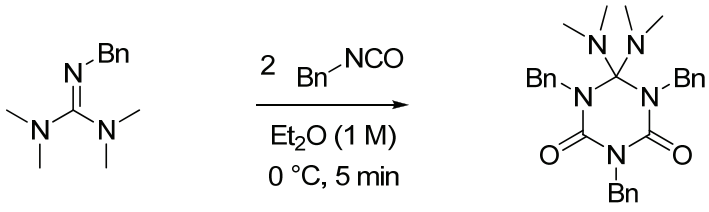
Chemical Formula: $C_{30}H_{33}N_5O_2$
Molecular Weight: 495,62

Following the general procedure above, a mixture of BnTBD **1b** (351 mg, 2.53 mmol) and benzylisocyanate (366 µL, 2.98 mmol) provided after crystallization the expected guanidine adduct **2c** as a colorless solid (492 mg, 67 %).

Mp = 110-112 °C (Et_2O); IR (neat): ν = 2940, 1693, 1653, 1475, 1455, 749, 702 cm^{-1}; ^1H NMR (CD_2Cl_2, 600 MHz): δ = 7.38 (d, J = 7.5 Hz, 2H), 7.32 (d, J = 7.4 Hz, 2H), 7.29 (t, J = 7.4 Hz, 4H), 7.25 – 7.15 (m, 5H), 7.10 (d, J = 7.5 Hz, 2H), 4.98 (q, J = 14.4 Hz, 2H), 4.90 (d, J = 14.3 Hz, 1H), 4.71 (d, J = 14.3 Hz, 1H), 4.53 (dd, J = 14.1, 9.2 Hz, 1H), 3.45 (s, 2H), 3.29 – 3.23 (m, 1H), 3.19 – 3.08 (m, 1H), 3.00–2.95 (m, 1H), 2.78 – 2.69 (m, 2H), 2.63 – 2.56 (m, 1H), 2.34 (dd, J = 14.5, 8.2 Hz, 1H), 2.11 – 2.02 (m, 1H), 2.00 – 1.89 (m, 1H), 1.87 – 1.79

(m, 1H), 1.78 – 1.70 ppm (m, 1H), ^{13}C NMR (CD_2Cl_2, 151 MHz): δ = 153.5, 151.5, 140.1, 138.8, 138.5, 128.9, 128.7, 128.6, 128.5, 128.3, 127.4, 127.4, 127.0, 98.2, 52.5, 47.2, 46.4, 45.2, 43.9, 42.6, 36.4, 23.3, 20.7 ppm; HRMS (ESI): m/z calcd for $C_{30}H_{34}N_5O_2$ $[M+H]^+$: 496.27125, found: 496.2711.

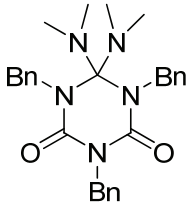
- **Synthesis of guanidine derivative 2d**



3 **2d**, 92 %

Benzylisocyanate (178 µL, 1.45 mmol) was added dropwise to a solution of benzyltetramethyl guanidine **3** (153 mg, 745 µmol) in Et_2O (1 mL) at 0 °C. The homogeneous reaction mixture was stirred 5 min at 0 °C. The solvent was then evaporated and the crude mixture was filtrated through a short plug of silica gel (Et_2O) to afford the expected product **2d** as a white foam (315 mg, 92 %).

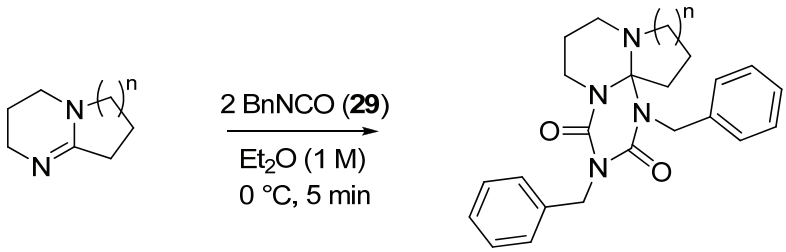
➢ 1,3,5-tribenzyl-6,6-bis(dimethylamino)-1,3,5-triazinane-2,4-dione (**2d**)



Chemical Formula: $C_{28}H_{33}N_5O_2$
Molecular Weight: 471,59

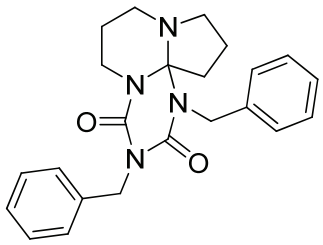
IR (neat): ν = 2939, 1691, 1655, 1497, 1393, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.59 – 7.53 (m, 2 H), 7.40 – 7.15 (m, 13 H), 5.18 (s, 2 H), 4.77 (s, 4 H), 2.25 ppm (s, 12 H), ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 153.4, 138.0, 137.8, 128.9, 128.3, 128.2, 127.3, 127.0, 126.5, 104.0, 47.3, 45.4, 38.4 ppm; HRMS (ESI): m/z calcd for $C_{28}H_{34}N_5O_2$ $[M+H]^+$: 472.27125, found: 472.2708.

- **General procedure for the synthesis of amidine derivatives 4a-b**



Benzylisocyanate (1.9 mmol) was added dropwise to a solution of amidine (1 mmol) in Et_2O (1 mL) at 0 °C. The homogeneous reaction mixture was then stirred 5 min at 0 °C. After recrystallization of the crude mixture at –40 °C, the crystals were filtered and washed with a small amount of ether affording the expected compound as a colorless solid.

➢ DBN-2 BnNCO adduct **4a**



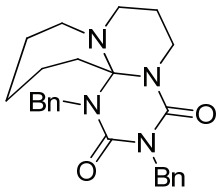
Chemical Formula: $C_{23}H_{26}N_4O_2$
Molecular Weight: 390,48

Following the general procedure above, a mixture of DBN (122 µL, 0.987 mmol) and benzylisocyanate (230 µL, 1.88 mmol) provided after crystallization the expected amidine adduct **4a** as a colorless solid (634 mg, 89%).

Monocrystals were grown by slow evaporation of a THF solution of **4a** at room temperature for XRD structure determination.

Mp = 158–159 °C (toluene); IR (neat): ν = 2949, 1697, 1655, 1470, 1453, 701 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz): δ = 7.42 – 7.15 (m, 10H), 4.99 (AB, J = 11.6 Hz, 2H), 4.63 (AB, J = 35.4 Hz, 2H), 4.25 (ddd, J = 1.3 Hz, J = 10.0 Hz, J = 14.1 Hz, 1H), 3.18 – 3.01 (m, 2H), 2.83 – 2.53 (m, 3H), 2.22 – 2.12 (m, 2H), 2.06 – 1.89 (m, 1H), 1.84 – 1.69 (m, 2H), 1.69 – 1.52 ppm (m, 1H), ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 154.2, 152.4, 140.2, 139.5, 128.6, 128.5, 128.3, 128.0, 127.2, 127.1, 92.1, 51.0, 45.9, 45.0, 38.5, 38.1, 33.9, 22.7, 19.6 ppm; HRMS (ESI): m/z calcd for $C_{23}H_{26}N_4O_2Na$ $[M+Na]^+$: 413.19535; found: 441.1951.

➢ DBU-2 BnNCO adduct **4b**



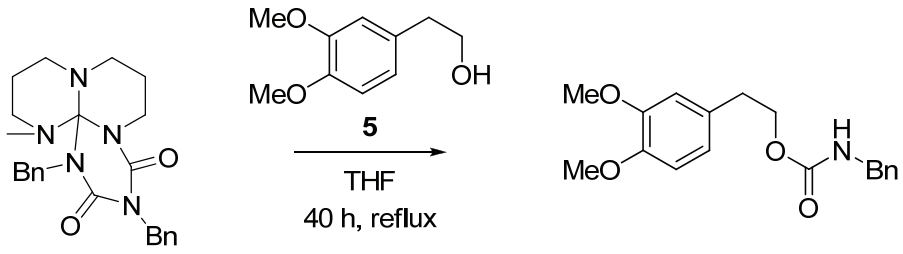
Chemical Formula: $C_{25}H_{30}N_4O_2$
Molecular Weight: 418,53

Following the general procedure above, a mixture of DBU (148 µL, 0.987 mmol) and benzylisocyanate (230 µL, 1.88 mmol) provided after crystallization the expected amidine adduct **4b** as a colorless solid (335 mg, 85%).

Monocrystals were grown by slow evaporation of a THF solution of **4b** at room temperature for XRD structure determination.

Mp = 146-148 °C (toluene); IR (neat): ν = 2930, 1695, 1654, 1465, 1453, 699 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz): δ = 7.42 – 7.15 (m, 10H), 4.99 (AB, J = 17.4 Hz, 2H), 4.97 (d, J = 14.7 Hz, 1H), 4.71 (d, J = 17.4 Hz, 1H), 4.34 (ddd, J = 1.3 Hz, J = 9.8 Hz, J = 13.9 Hz, 1H), 3.20 – 2.97 (m, 2H), 2.96 – 2.83 (m, 1H), 2.69 – 2.54 (m, 1H), 2.45 – 2.34 (m, 1H), 2.21 – 1.96 (m, 2H), 1.93 – 1.53 (m, 7H), 1.48 – 1.31 ppm (m, 1H), ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 154.2, 151.6, 140.1, 139.5, 128.6, 128.5, 128.3, 128.2, 127.3, 127.1, 91.4, 52.5, 47.2, 45.9, 45.1, 36.2, 35.2, 31.8, 29.8, 23.1, 21.7 ppm; HRMS (ESI): m/z calcd for $C_{25}H_{30}N_4O_2Na$ $[M+Na]^+$: 441.22665; found: 441.2269.

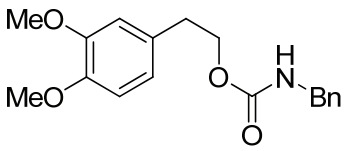
• Reaction of adduct 2a with 3,4-dimethoxyphenethyl alcohol



2a **6**, 87 %

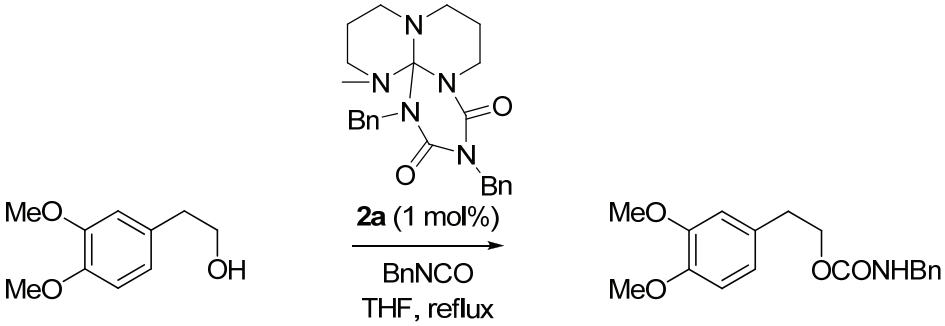
To a solution of adduct **2a** (210 mg, 0.5 mmol) in THF (5 mL) was added 3,4-dimethoxyphenethyl alcohol **5** (182 mg, 1 mmol). The mixture was stirred 40 h under reflux. The reaction was then quenched with water (10 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The organic layers were dried over Na_2SO_4 and the solvents were evaporated under vacuum. Purification on silica gel (petroleum ether/ethyl acetate: 7/3) afforded the desired carbamate **6** as a white solid (274 mg, 87 %).

➢ 3,4-dimethoxyphenethyl benzylcarbamate **6**



R_f: 0.41 (petroleum ether/ethyl acetate: 7/3); IR (neat): = 3332, 2917, 1693, 1519, 1261, 1139 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.37 – 7.23 (m, 5H), 6.83 – 6.71 (m, 3H), 5.02 (br s, 1H), 4.36 (d, *J* = 5.6 Hz, 2H), 4.30 (t, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 3.85 (s, 3H), 2.89 ppm (t, *J* = 7.1 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 156.3, 148.7, 147.5, 138.6, 130.3, 128.5, 127.3, 127.2, 120.7, 112.0, 111.2, 65.4, 55.7, 55.6, 44.8, 35.0 ppm; HRMS (ESI): m/z calcd for $C_{18}H_{21}NO_4Na$ $[M+Na]^+$: 338.1368; found: 338.1367.

- **Synthesis of carbamate 6 catalyzed by guanidine derivative 2a**

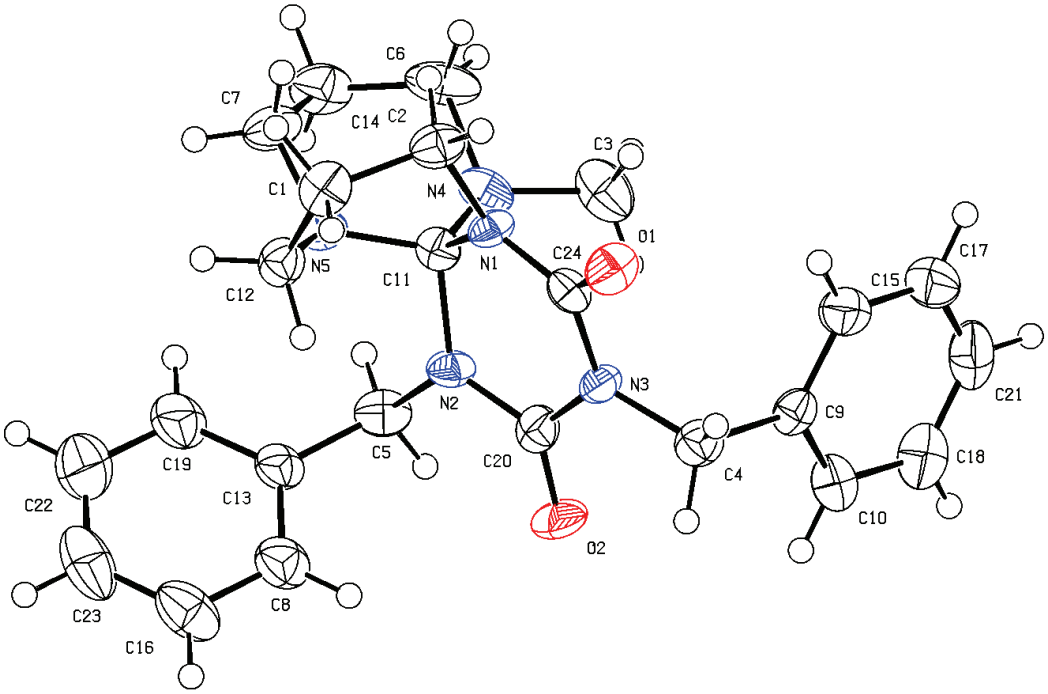


5 **6**, 84 %

To a solution of 3,4-dimethoxyphenethyl alcohol **5** (149 mg, 0.8 mmol) in THF (3 mL) was added benzylisocyanate (100 µL, 0.8 mmol) followed by the addition of a solution of catalyst **2a** (3.4 mg, 8 µmol) in THF (1 mL). The mixture was stirred 24 h under reflux. The reaction was then quenched with water (10 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The organic layers were dried over Na_2SO_4 and the solvents were evaporated under vacuum. Purification on silica gel (petroleum ether/ethyl acetate: 7/3) afforded the desired carbamate **6** as a white solid (212 mg, 84 %).

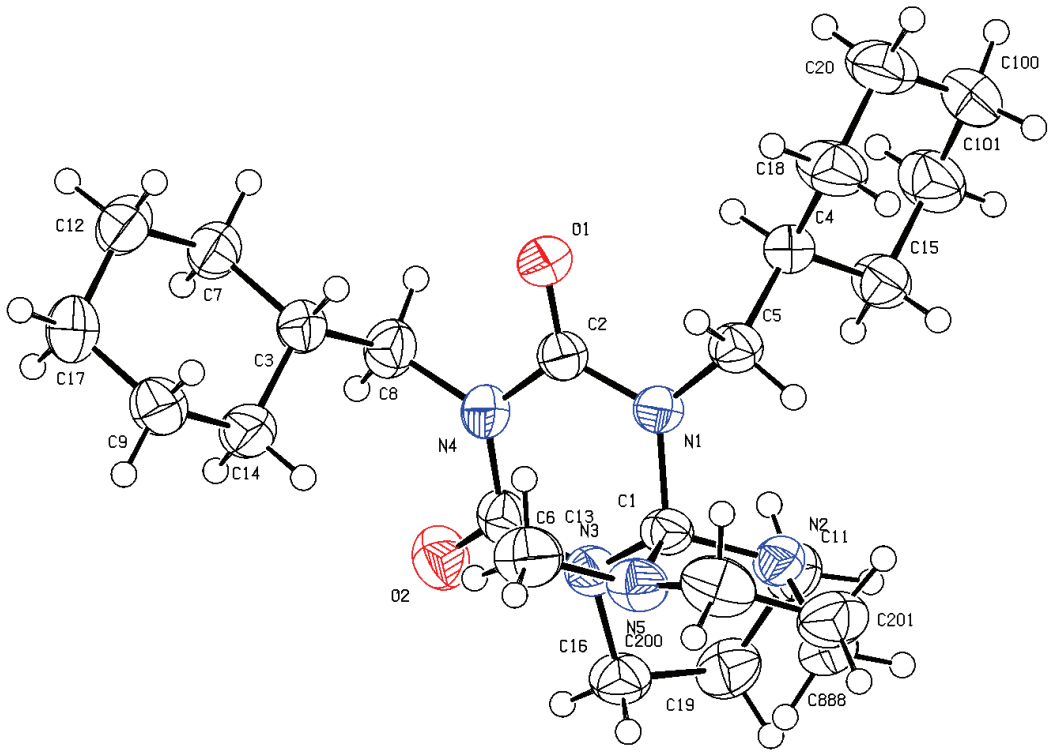
- **Crystallographic data**

  - MTBD-2 BnNCO adduct **2a**



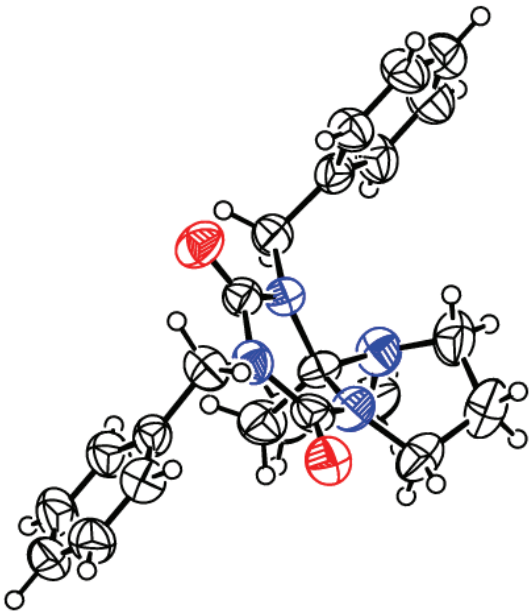
Compound reference	MTBD - 2 BnNCO
Chemical formula	$C_{24}H_{29}N_5O_2$
Formula Mass	419.52
Crystal system	Orthorhombic
a/Å	12.5135(7)
b/Å	8.2914(4)
c/Å	41.841(2)
α/°	90.00
β/°	90.00
γ/°	90.00
Unit cell volume/Å^3	4341.2(4)
Temperature/K	200
Space group	*Pbca*
No. of formula units per unit cell, *Z*	8
Radiation type	CuKα
Absorption coefficient, μ/mm^{-1}	0.673
No. of reflections measured	27580
No. of independent reflections	1803
R_{int}	0.0506
Final R_1 values ($I > 2\sigma(I)$)	0.0573
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1516
Final R_1 values (all data)	0.0751
Final $wR(F^2)$ values (all data)	0.1697
Goodness of fit on F^2	1.266
CCDC number	905749

➢ MTBD-2 CycCH_2NCO adduct **2b**



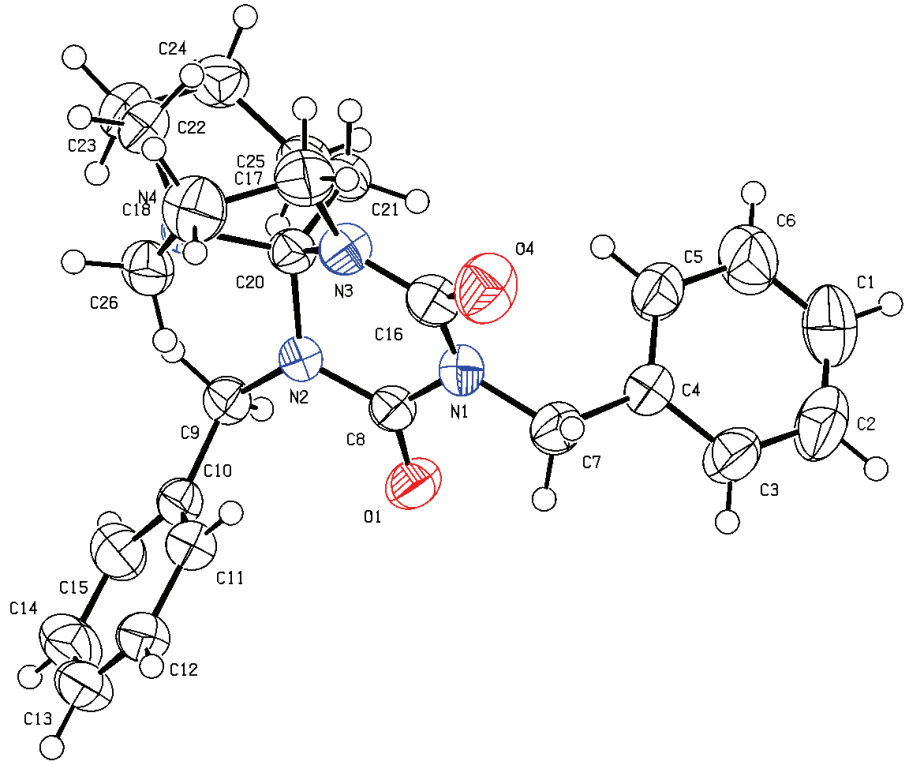
Compound reference	MTBD - 2 CyMeNCO
Chemical formula	$C_{24}H_{41}N_5O_2$
Formula Mass	431.62
Crystal system	Triclinic
a/Å	9.0279(8)
b/Å	11.0405(12)
c/Å	12.5422(11)
α/°	71.337(6)
β/°	88.704(6)
γ/°	79.678(7)
Unit cell volume/Å^3	1164.40(19)
Temperature/K	293(2)
Space group	$P\bar{1}$,
No. of formula units per unit cell, *Z*	2
Radiation type	CuKα
Absorption coefficient, μ/mm^{-1}	0.628
No. of reflections measured	16534
No. of independent reflections	4183
R_{int}	0.0277
Final R_1 values ($I > 2\sigma(I)$)	0.0614
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1444
Final R_1 values (all data)	0.0652
Final $wR(F^2)$ values (all data)	0.1487
Goodness of fit on F^2	1.183
CCDC number	905750

➢ DBN-2 BnNCO adduct **4a**



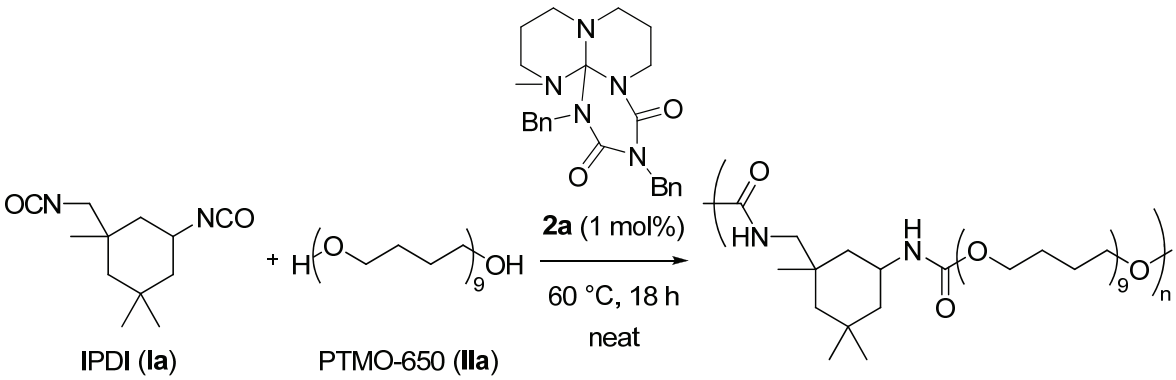
Compound reference	DBN-2 BnNCO
Chemical formula	$C_{138}H_{156}N_{24}O_{12}$
Formula Mass	2342.87
Crystal system	Monoclinic
a/Å	17.848(4)
b/Å	16.102(3)
c/Å	22.302(5)
α/°	90.00
β/°	110.45(3)
γ/°	90.00
Unit cell volume/Å^3	6005(2)
Temperature/K	150(2)
Space group	*Pc*
No. of formula units per unit cell, *Z*	2
Radiation type	CuKα
Absorption coefficient, μ/mm^{-1}	0.676
No. of reflections measured	81357
No. of independent reflections	18413
R_{int}	0.0267
Final R_1 values ($I > 2\sigma(I)$)	0.0601
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1610
Final R_1 values (all data)	0.1003
Final $wR(F^2)$ values (all data)	0.2263
Goodness of fit on F^2	0.793
Flack parameter	0.2(2)
CCDC number	905747

➢ DBU-2 BnNCO adduct **4b**

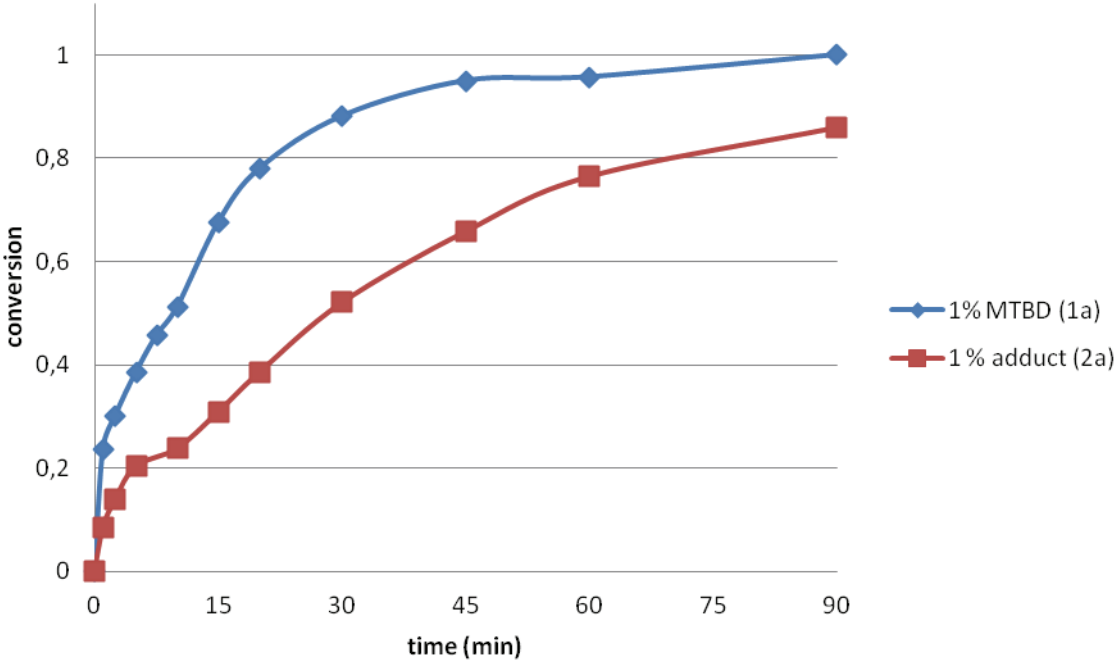


Compound reference	DBU-2 BnNCO
Chemical formula	$C_{25}H_{30}N_4O_2$
Formula Mass	418.53
Crystal system	Triclinic
a/Å	10.154(2)
b/Å	10.801(2)
c/Å	11.233(2)
α/°	69.90(3)
β/°	85.34(3)
γ/°	70.13(3)
Unit cell volume/Å^3	1087.2(4)
Temperature/K	150(2)
Space group	$P\bar{1}$,
No. of formula units per unit cell, *Z*	2
Radiation type	CuKα
Absorption coefficient, μ/mm^{-1}	0.656
No. of reflections measured	5116
No. of independent reflections	2106
R_{int}	0.0323
Final R_1 values ($I > 2\sigma(I)$)	0.0545
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1288
Final R_1 values (all data)	0.0619
Final $wR(F^2)$ values (all data)	0.1572
Goodness of fit on F^2	1.231
CCDC number	905748

- **Preliminary experiments of catalyzed PU synthesis from IPDI (Ia) and PTMO-650 (IIa)**

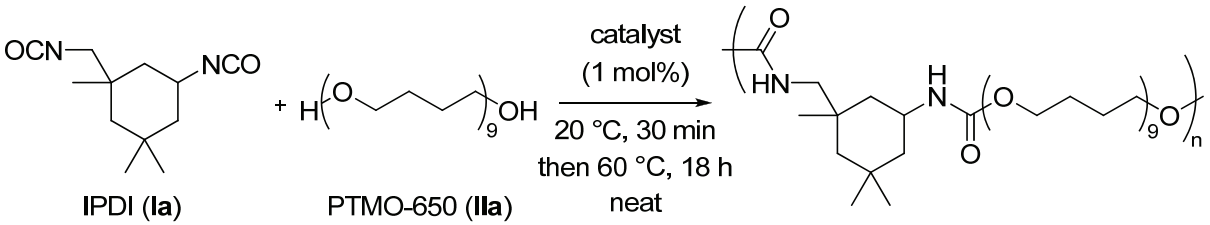


IPDI **Ia** (0.8 mL, 3.78 mmol) was added to a stoichiometric amount of PTMO-650 **IIa** (2.45 g, 3.78 mmol) at room temperature (water bath at 20 °C). A solution of catalyst (75.5 µmol) in THF (0.5 mL) was added and the flask was placed in an oil bath at 60 °C. The mixture was stirred 18 h at this temperature. Aliquots were taken and IR spectra were recorded to monitor the time course of the reaction.



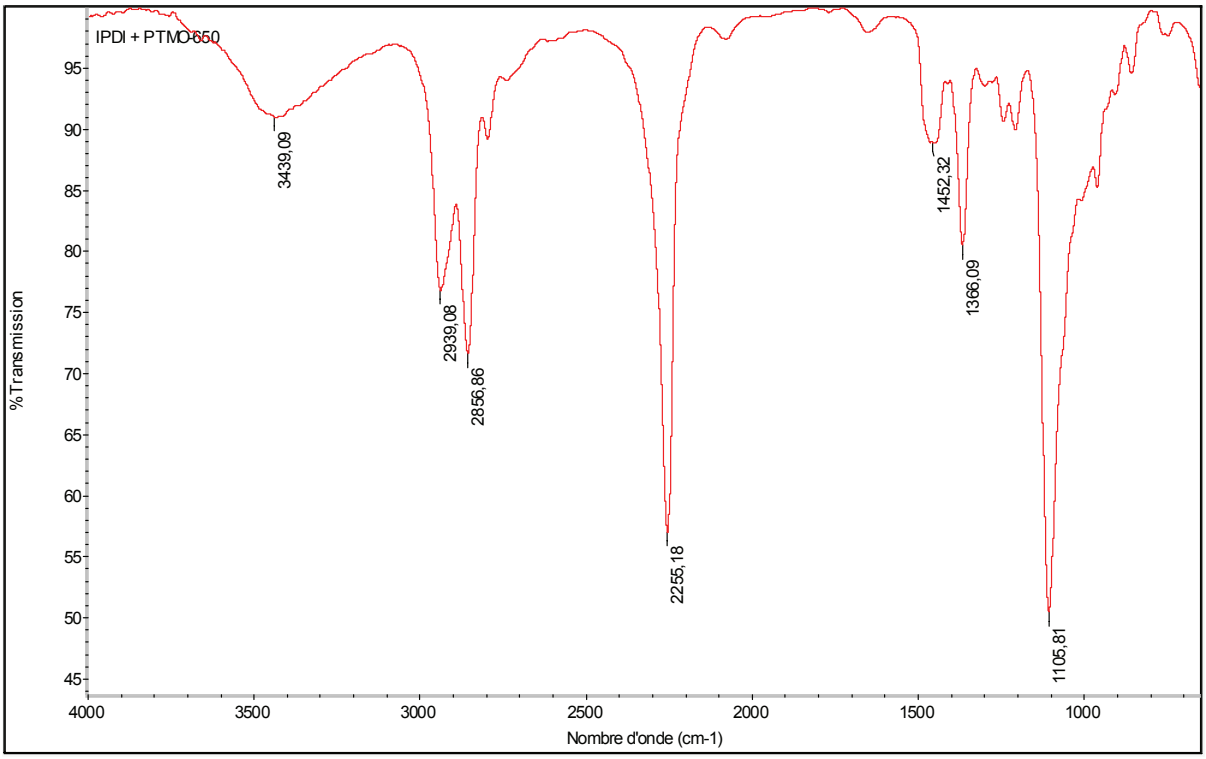
Time course of PU synthesis using MTBD **1a** (blue) or MTBD-2BnNCO **2a** (red) as catalyst

- **General procedure for the synthesis of PU from IPDI (Ia) and PTMO-650 (IIa)**

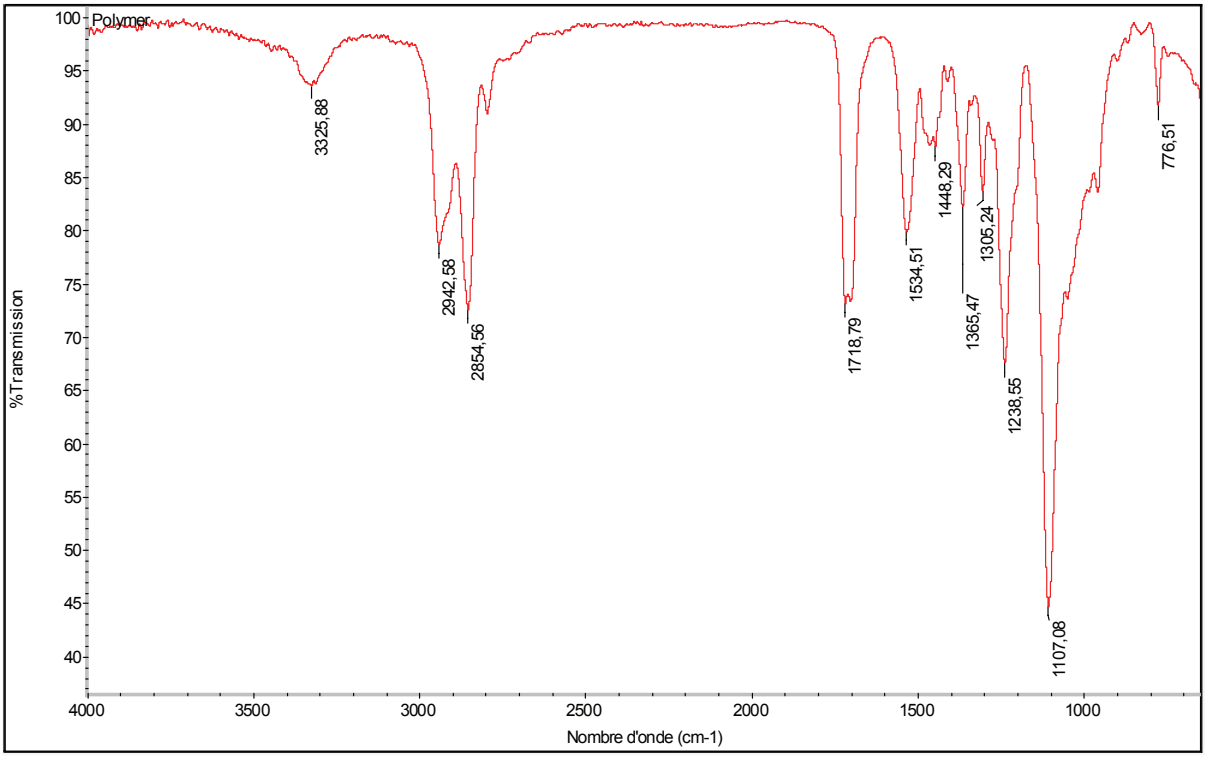


IPDI (0.8 mL, 3.78 mmol) was added to a stoichiometric amount of PTMO-650 (2.45 g, 3.78 mmol) at room temperature (water bath at 20 °C). A solution of catalyst (75.5 µmol) in THF (0.5 mL) was added dropwise and the mixture was stirred 30 min at 20 °C. The flask was then placed in an oil bath at 60 °C and the mixture was stirred 18 h at this temperature. Aliquots were taken and IR spectra were recorded to monitor the time course of the reaction. An aliquot is taken at the end of the reaction and quenched with methanol for SEC analysis.

- **Conversion monitoring during PU synthesis from IPDI (Ia) and PTMO-650 (IIa)**

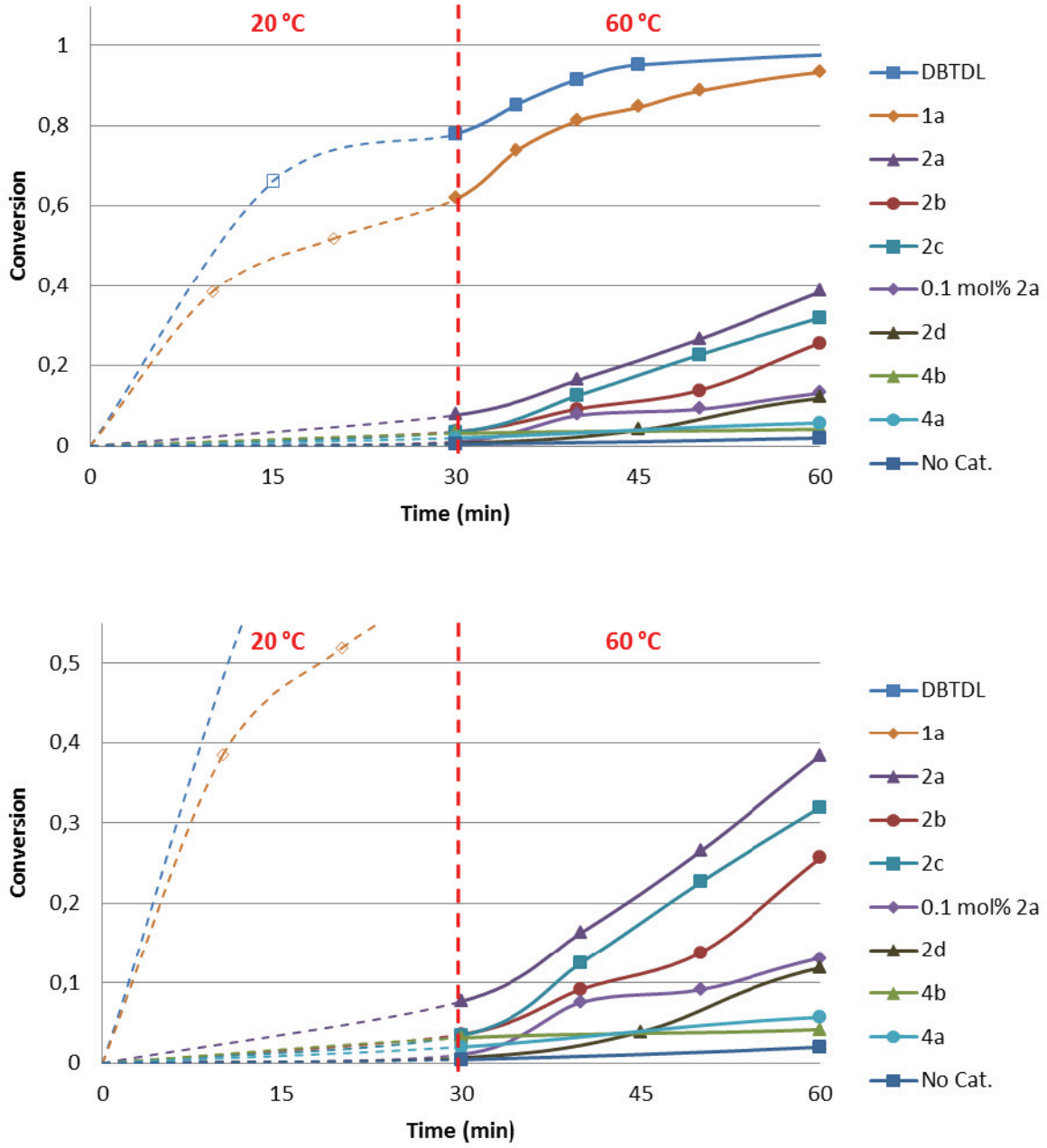


FT-IR spectrum of the starting mixture: IPDI **Ia** + PTMO-650 **IIa**



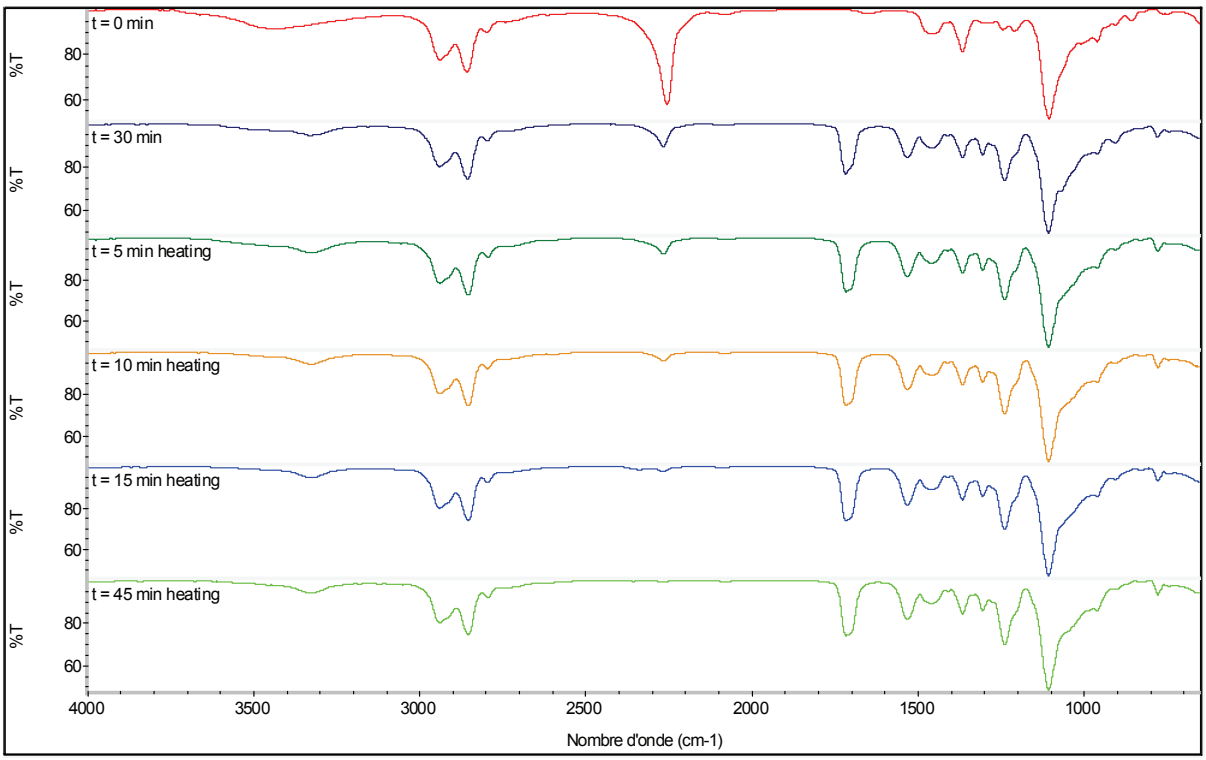
FT-IR spectrum of PU, obtained from IPDI **Ia** and PTMO-650 **IIa**

- **Zooms on the monitoring of the first hour conversion (*Figure 1*)**

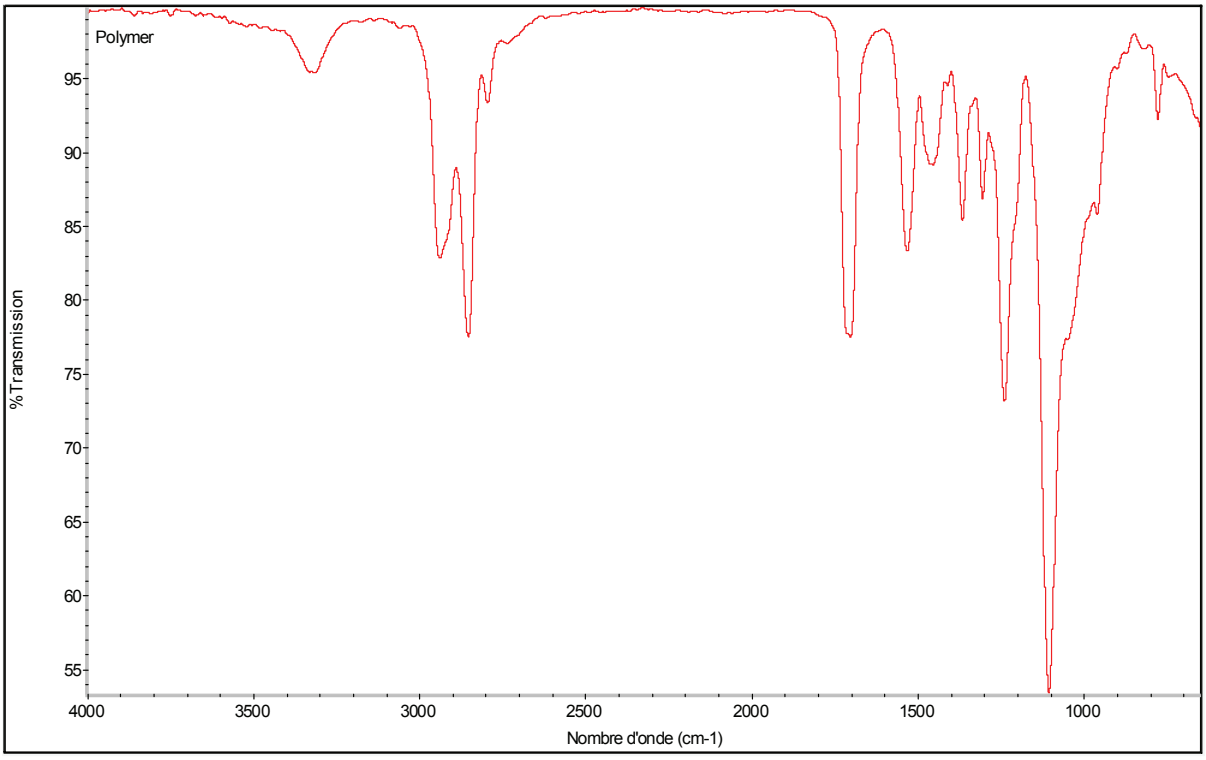


Polymerization of **Ia** and **IIa** with latent catalysts **2a-d** and **4a-b**.

➢ Synthesis of PU from **Ia** and **IIa** using DBTDL (1 mol%) as catalyst

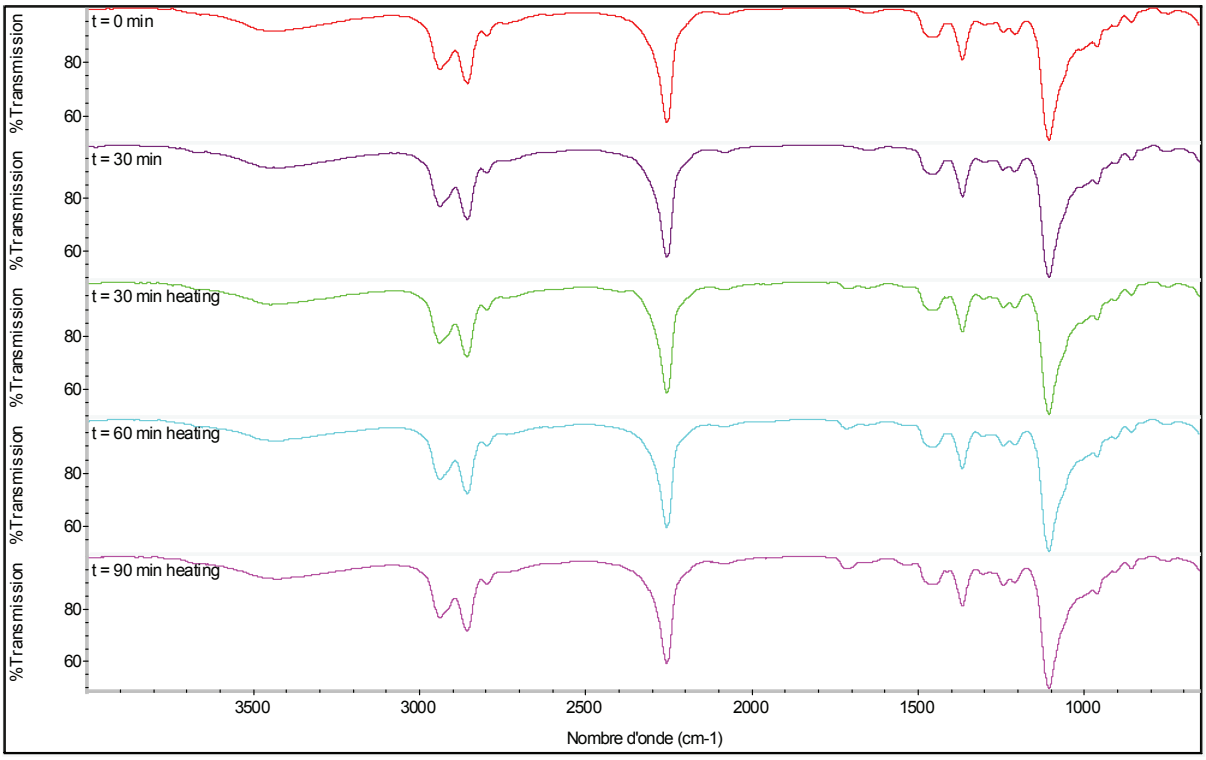


FT-IR spectra for the conversion monitoring (figure 1) using DBTDL as catalyst

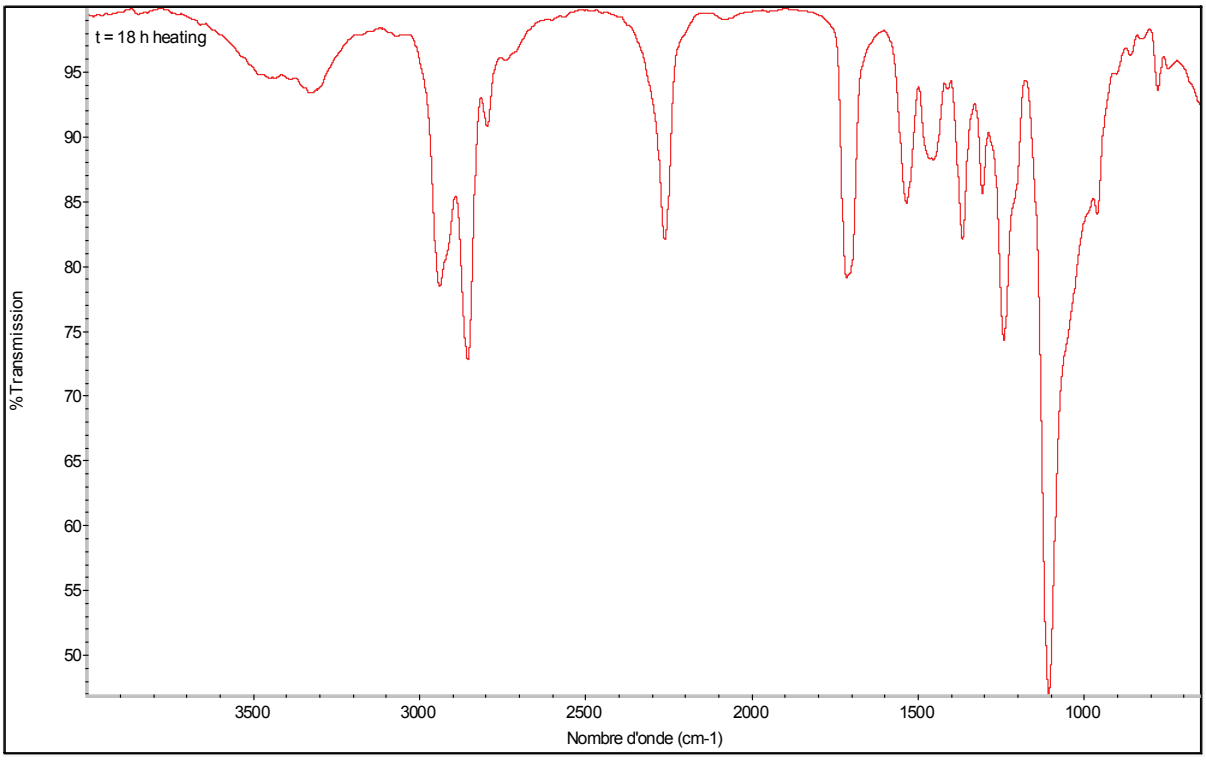


FT-IR spectrum of PU obtained using DBTDL as catalyst

➢ Synthesis of PU from **Ia** and **IIa** without catalyst

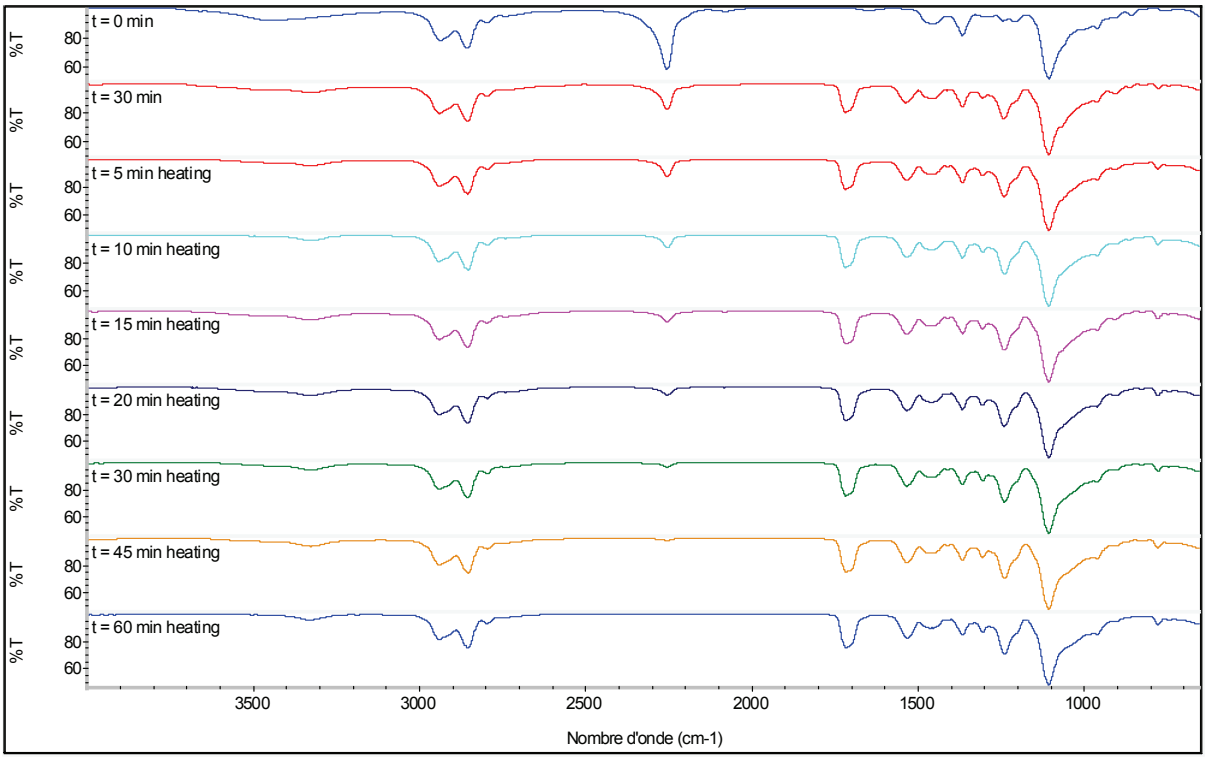


FT-IR spectra for the conversion monitoring (figure 1) without catalyst

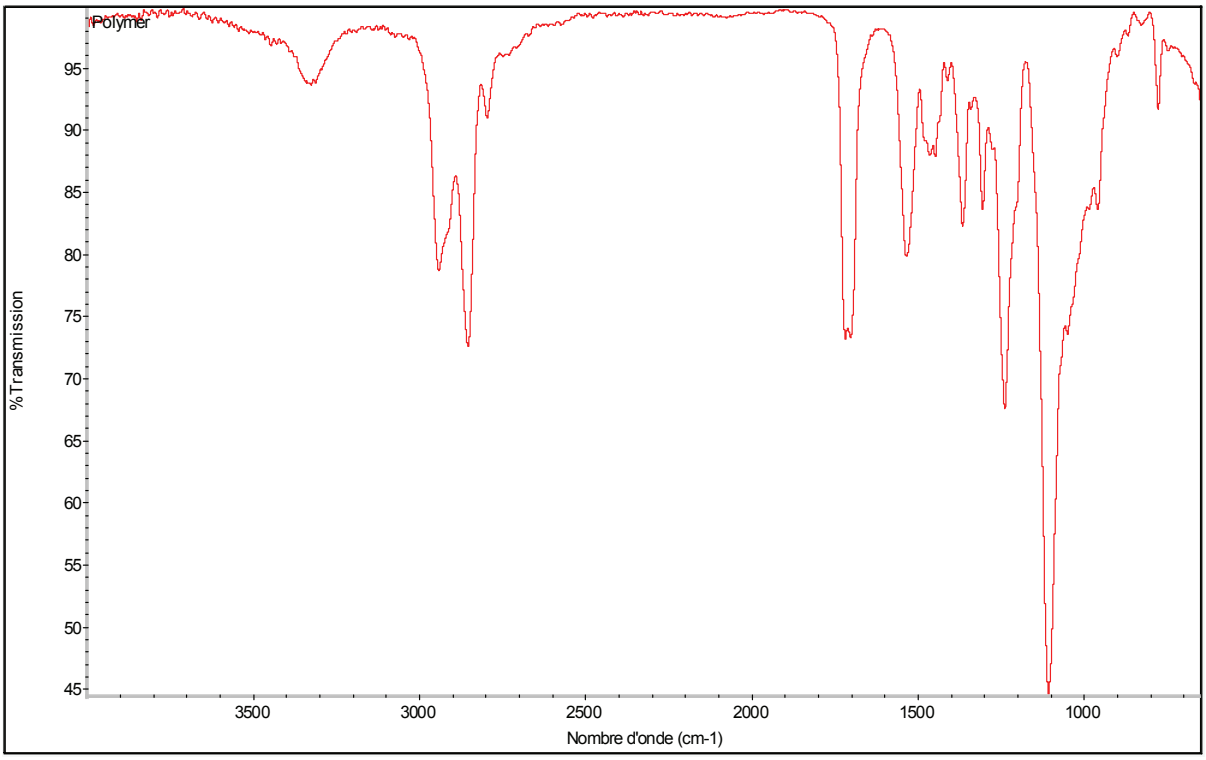


FT-IR spectrum of PU obtained without catalyst

➢ Synthesis of PU from **Ia** and **IIa** using MTBD **1a** (1 mol%) as catalyst

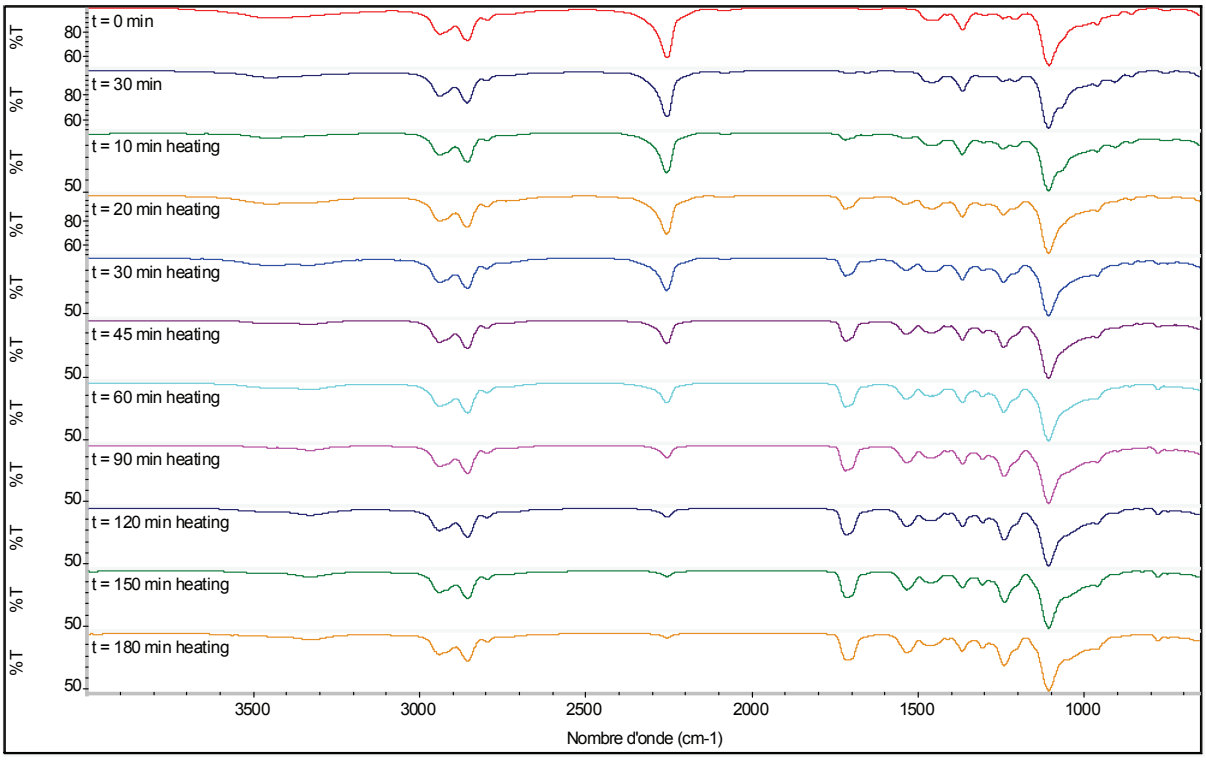


FT-IR spectra for the conversion monitoring (figure 1) using MTBD (**1a**) as catalyst

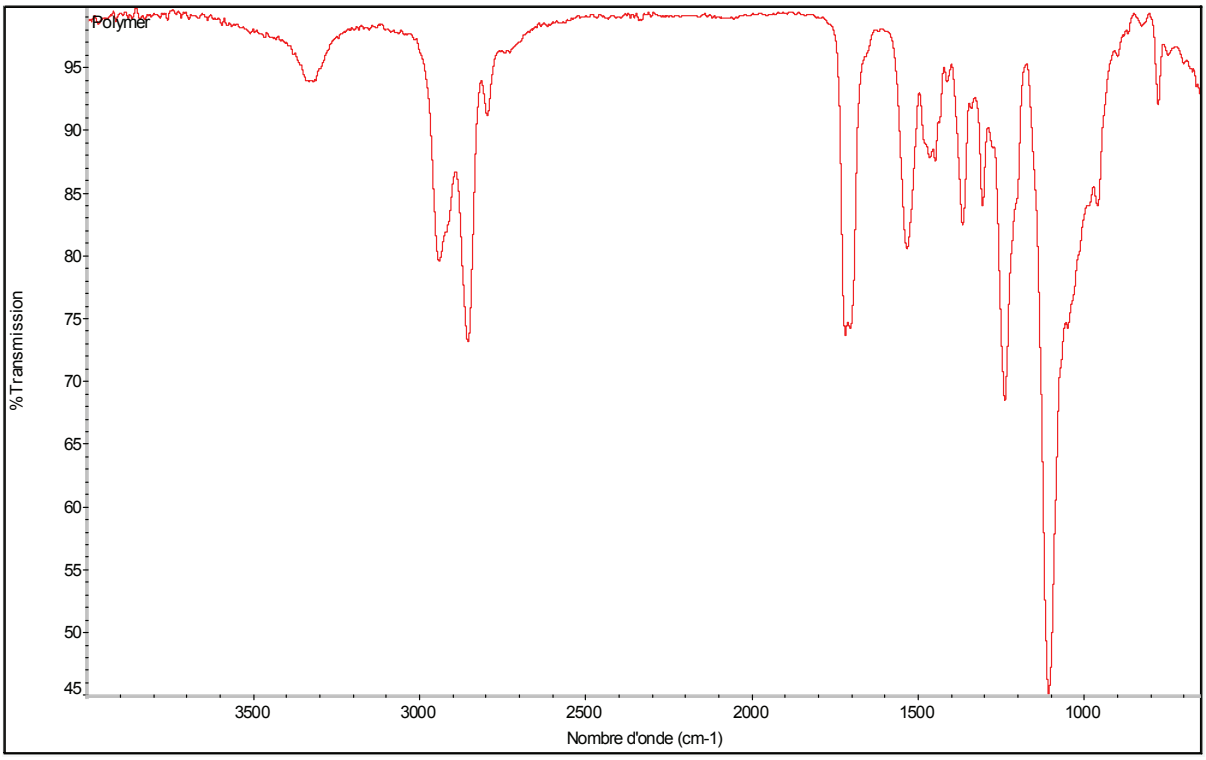


FT-IR spectrum of PU obtained using MTBD (**1a**) as catalyst

➢ Synthesis of PU from **Ia** and **IIa** using MTBD-2BnNCO **2a** (1 mol%) as catalyst

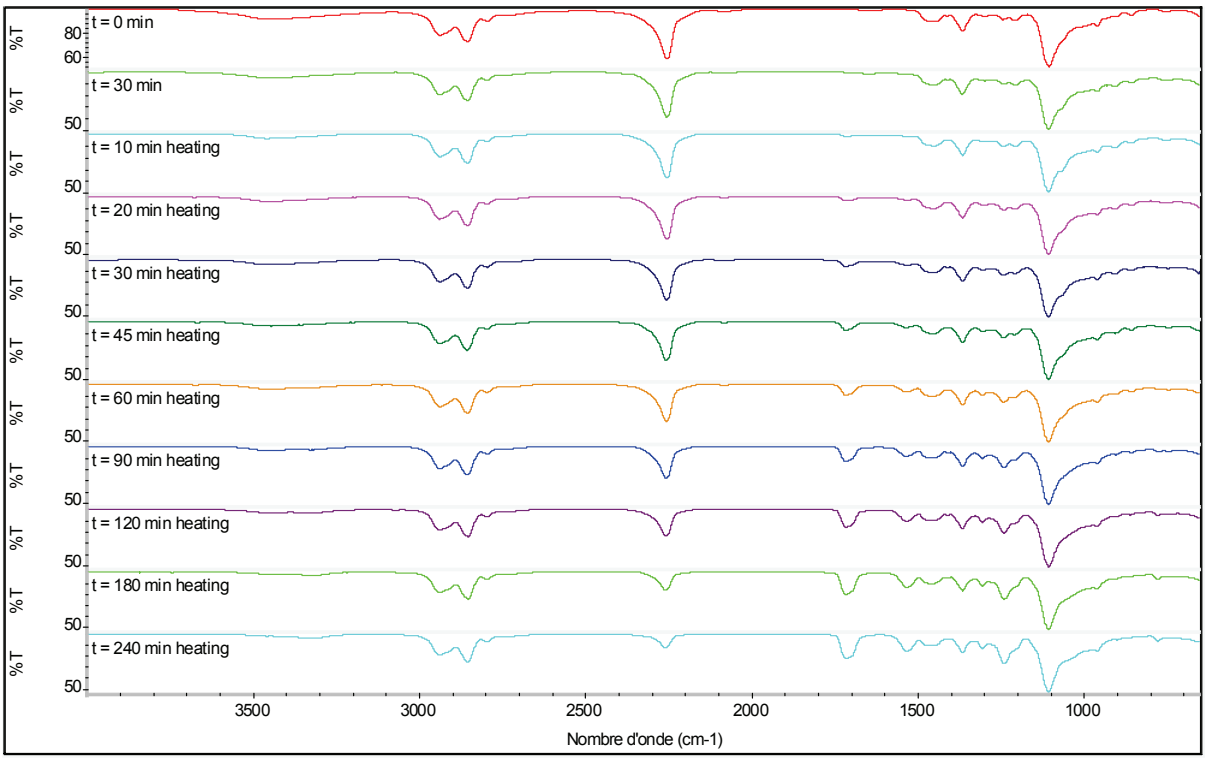


FT-IR spectra for the conversion monitoring (figure 1) using MTBD-2BnNCO (**2a**) as catalyst

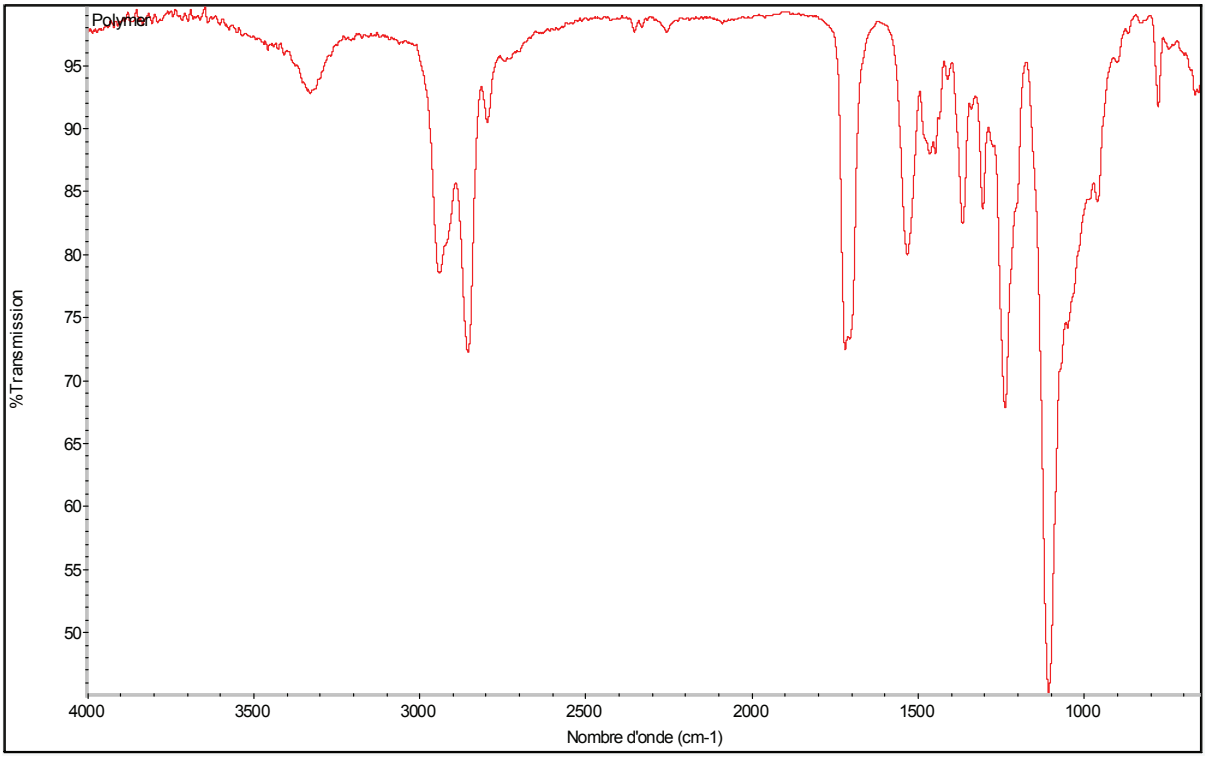


FT-IR spectrum of PU obtained using MTBD-2BnNCO (**2a**) as catalyst

➢ Synthesis of PU from **Ia** and **IIa** using MTBD-2BnNCO **2a** (0.1 mol%) as catalyst

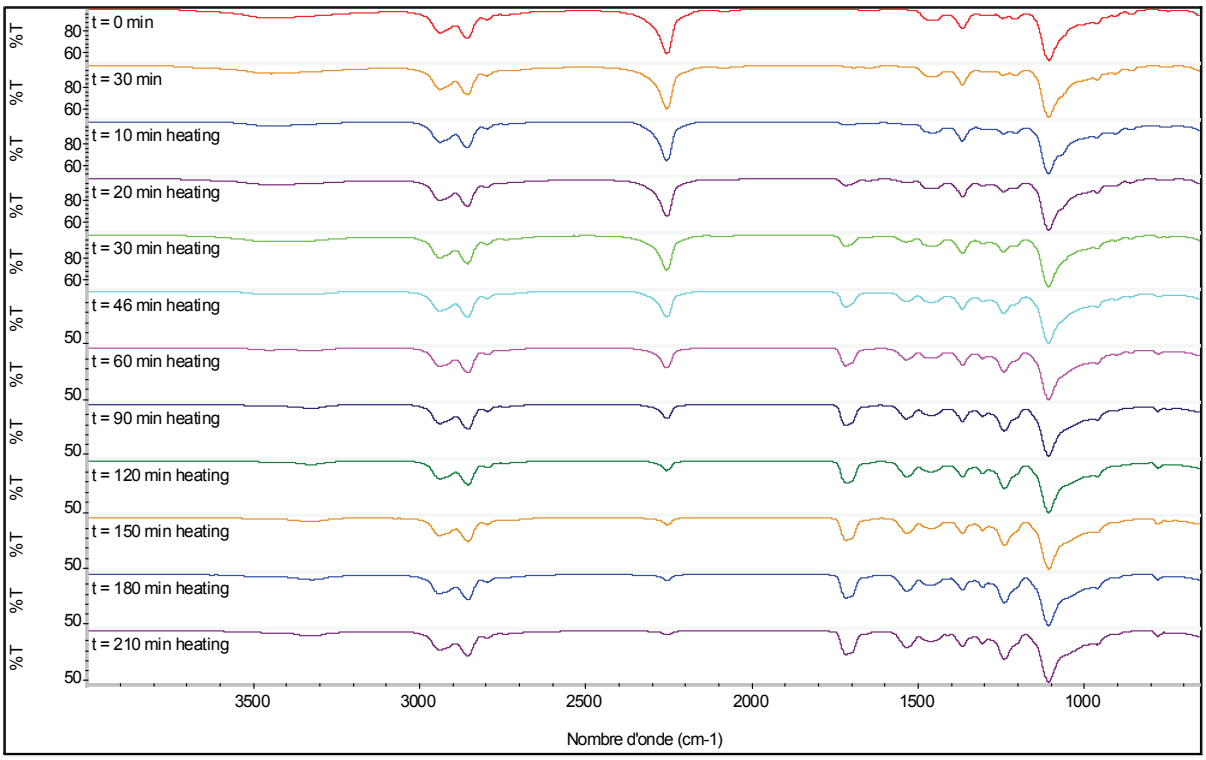


FT-IR spectra for the conversion monitoring (figure 1) using MTBD-2BnNCO (**2a**) as catalyst

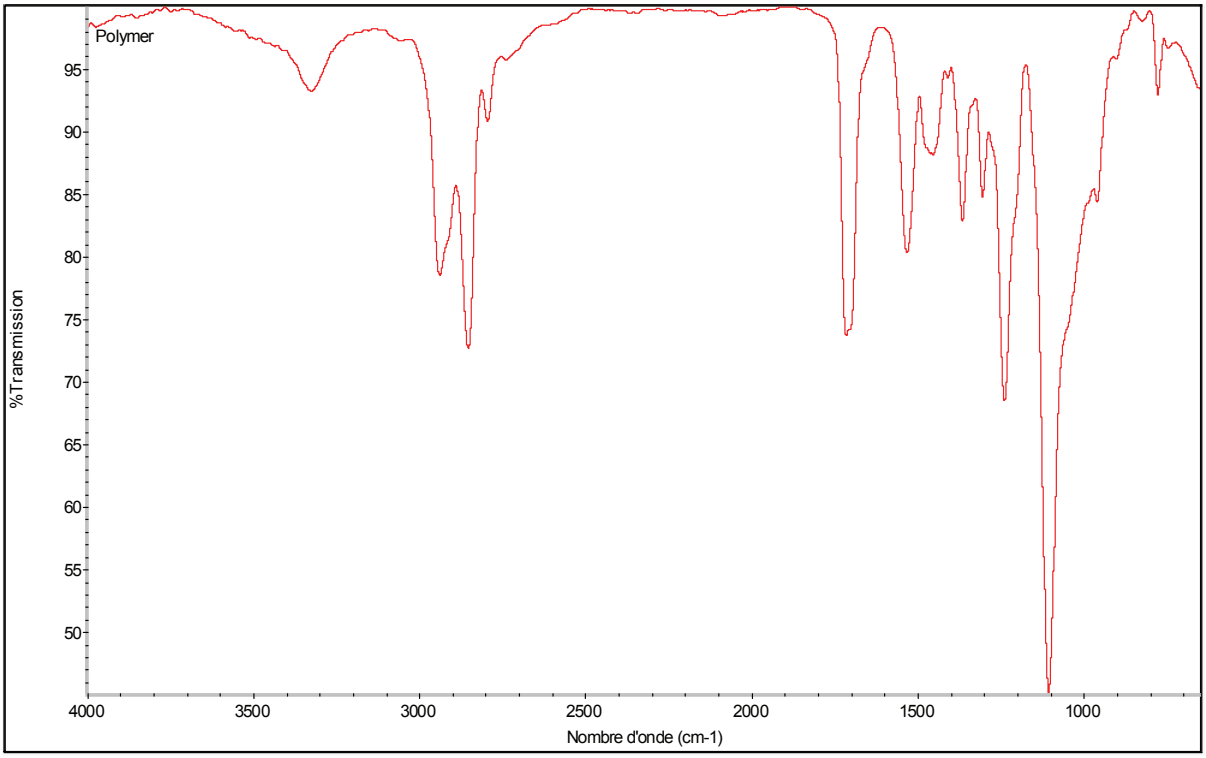


FT-IR spectrum of PU obtained using MTBD-2BnNCO (**2a**) as catalyst

➢ Synthesis of PU from **Ia** and **IIa** using MTBD-2CyMeNCO **2b** (1 mol%) as catalyst

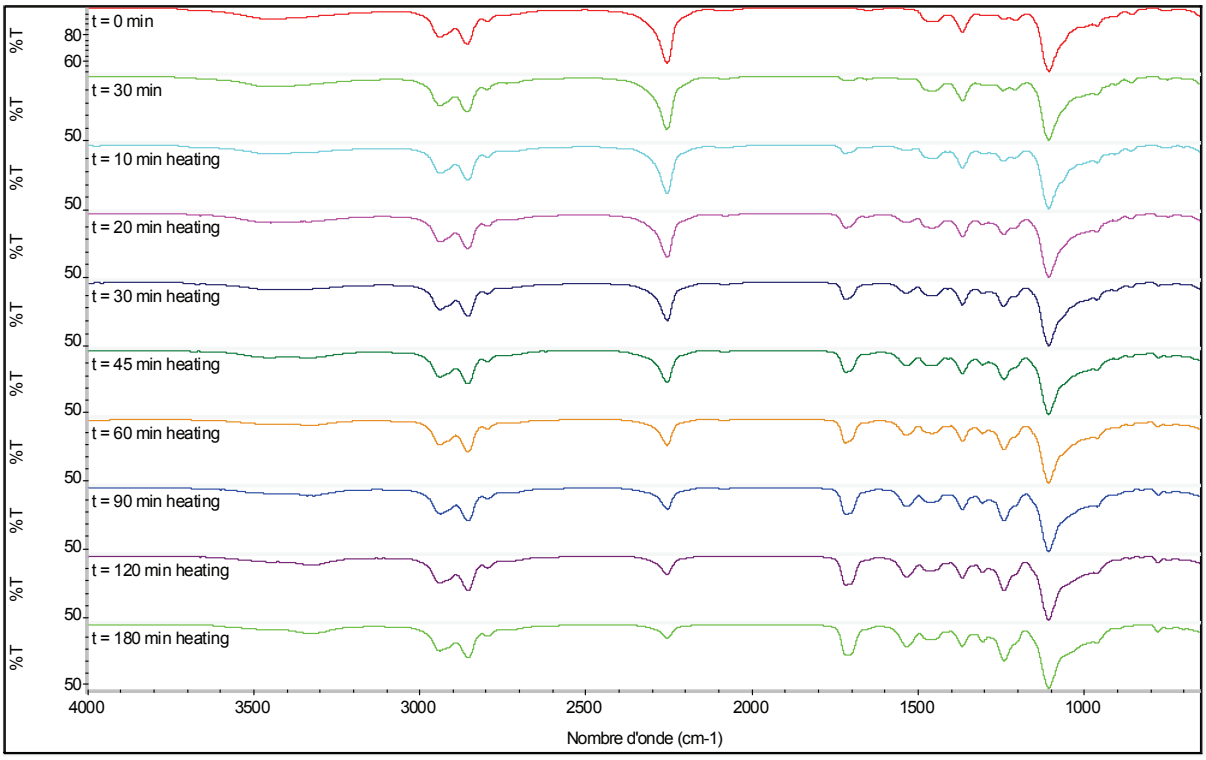


FT-IR spectra for the conversion monitoring (figure 1) using MTBD-2CycMeNCO (**2b**) as catalyst

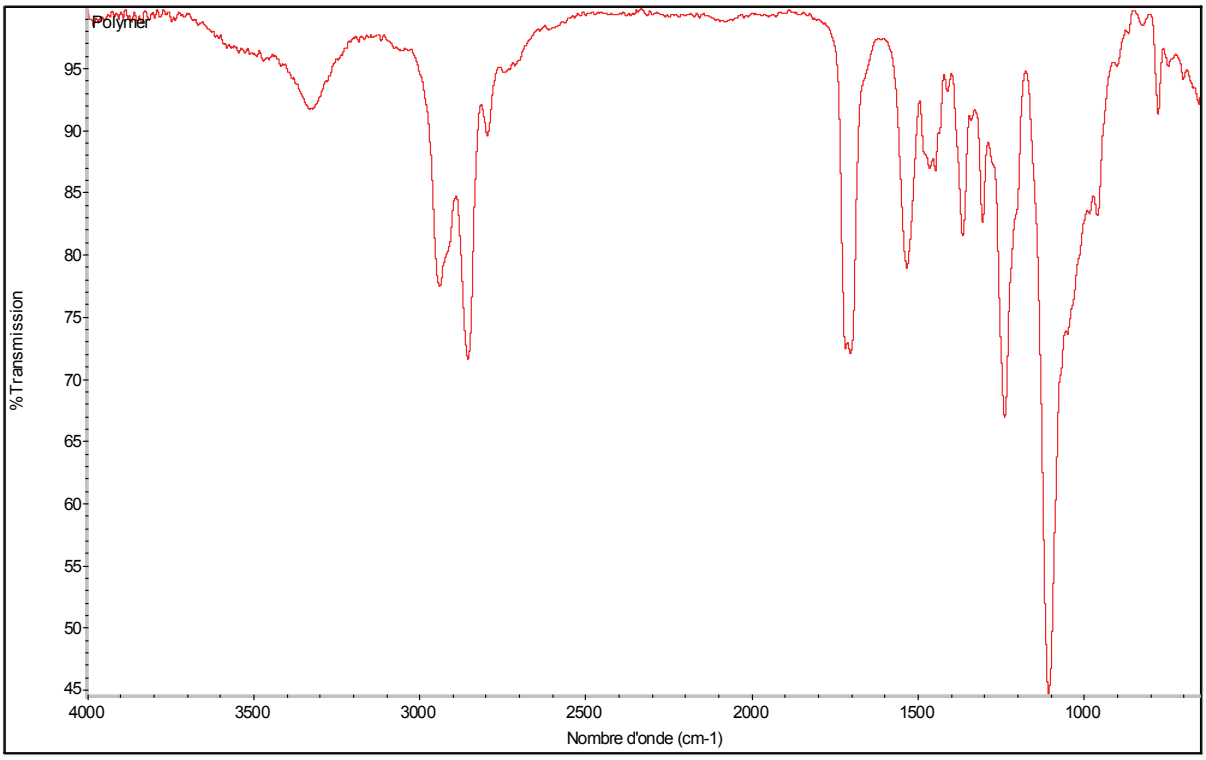


FT-IR spectrum of PU obtained using MTBD-2CycMeNCO (**2b**) as catalyst

➢ Synthesis of PU from **Ia** and **IIa** using BnTBD-2BnNCO **2c** (1 mol%) as catalyst

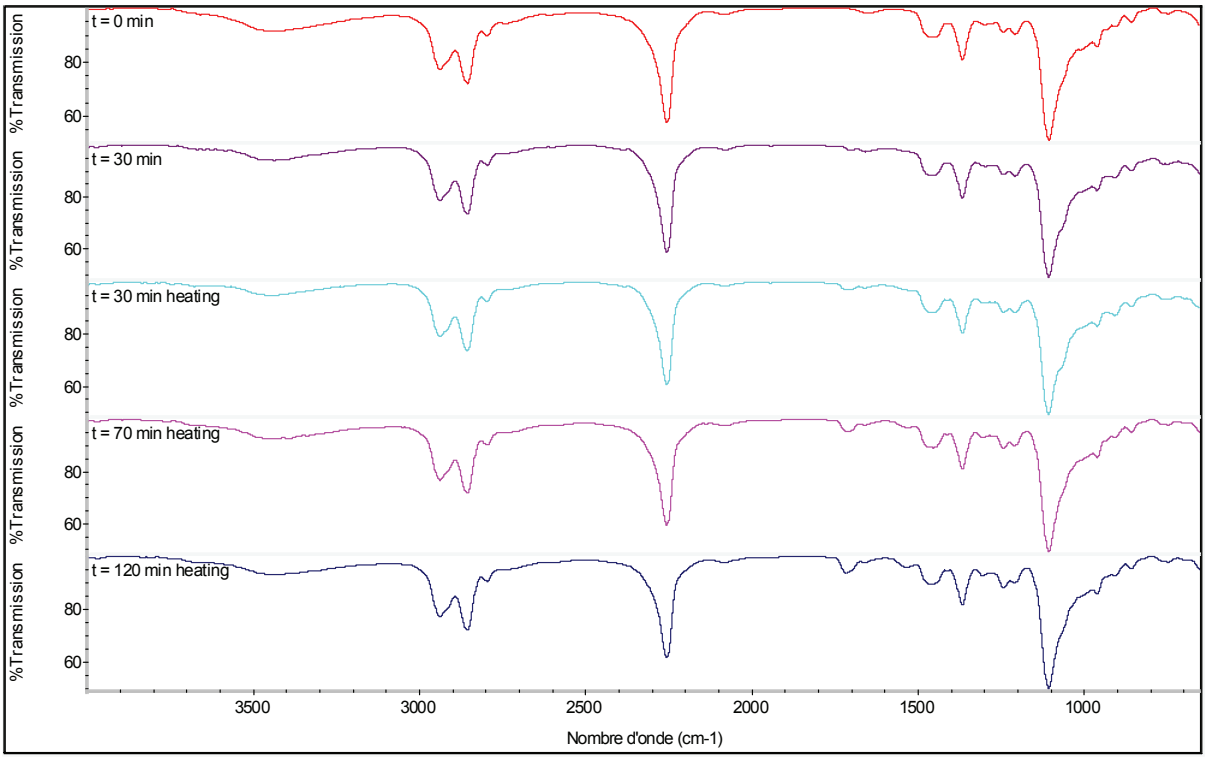


FT-IR spectra for the conversion monitoring (figure 1) using BnTBD-2BnNCO (**2c**) as catalyst

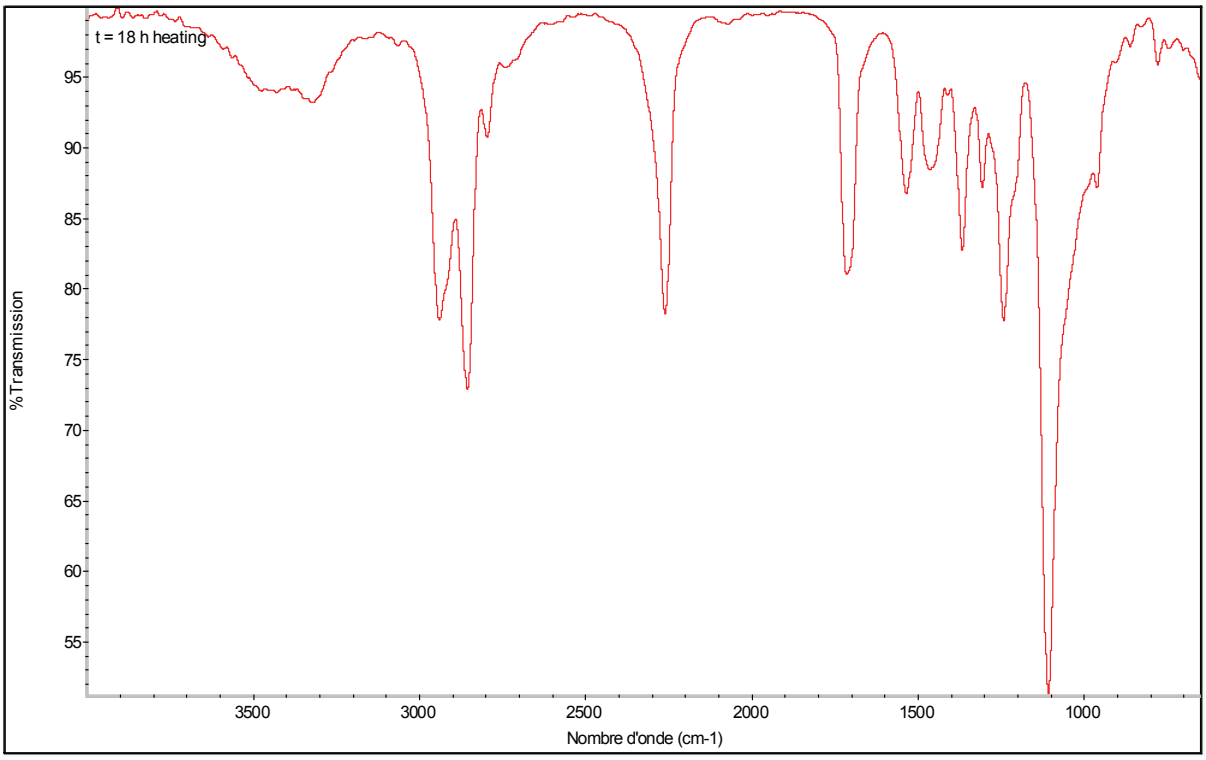


FT-IR spectrum of PU obtained using MTBD-2BnNCO (**2a**) as catalyst

➢ Synthesis of PU from **Ia** and **IIa** using DBN-2BnNCO **4a** (1 mol%) as catalyst

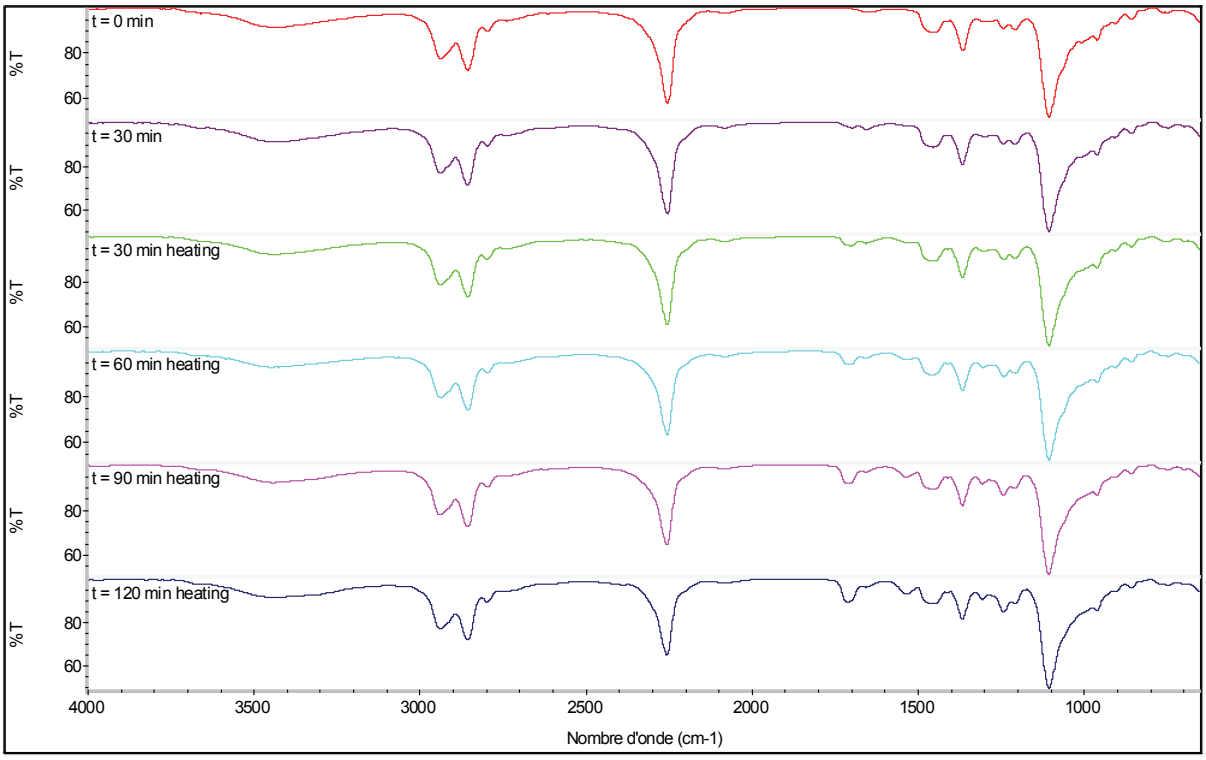


FT-IR spectra for the conversion monitoring (figure 1) using DBN-2BnNCO (**4a**) as catalyst

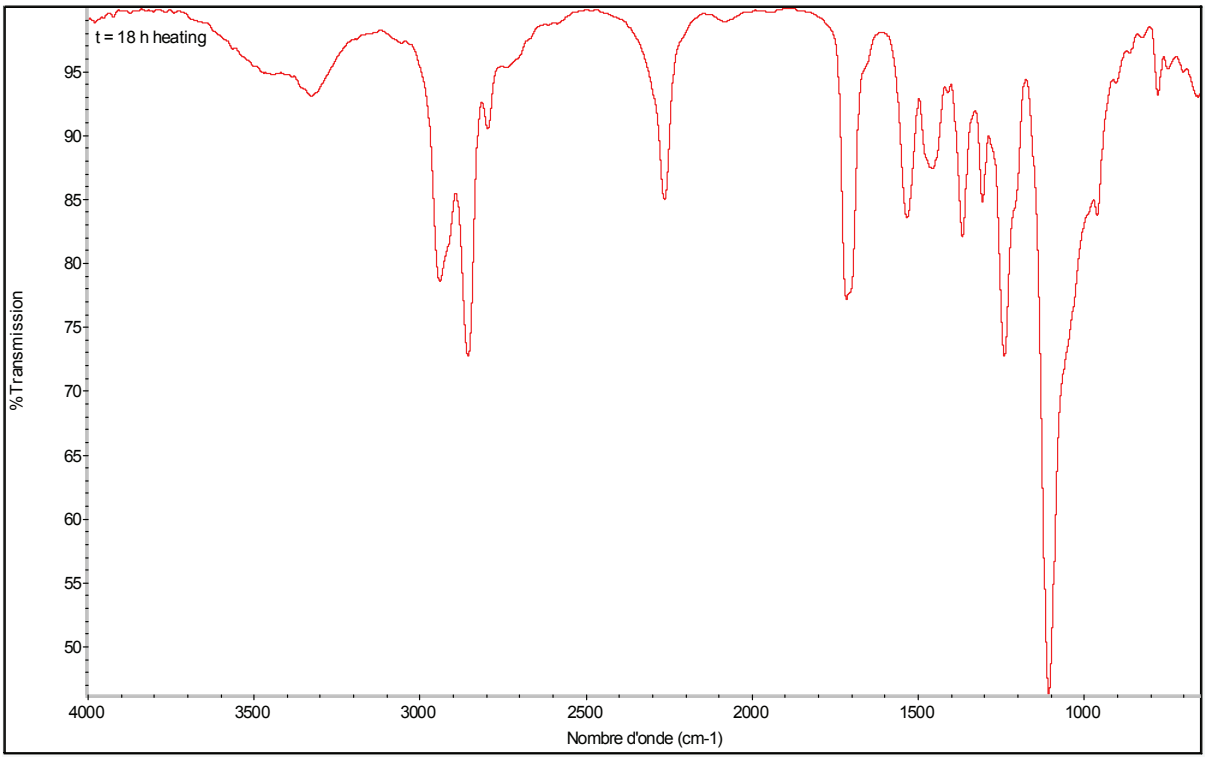


FT-IR spectrum of PU obtained using DBN-2BnNCO (**4a**) as catalyst

➢ Synthesis of PU from **Ia** and **IIa** using DBU-2BnNCO **4b** (1 mol%) as catalyst

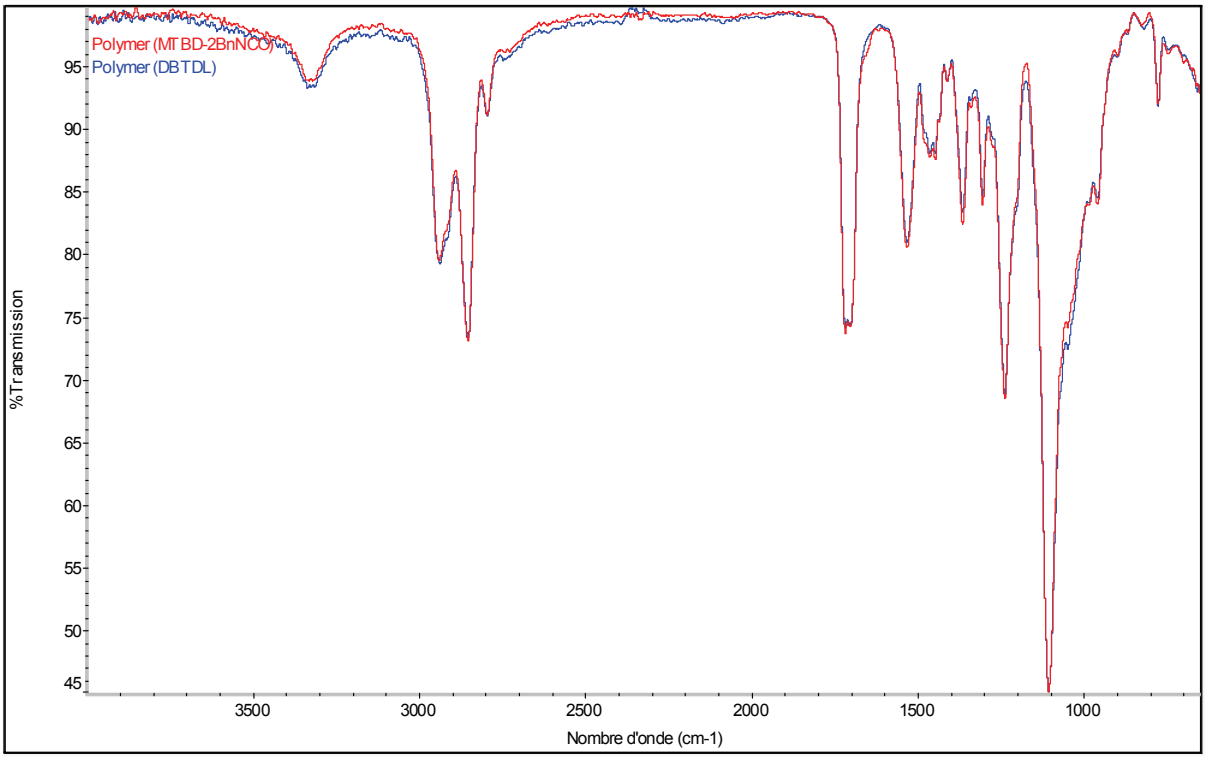


FT-IR spectra for the conversion monitoring (figure 1) using DBU-2BnNCO (**4b**) as catalyst



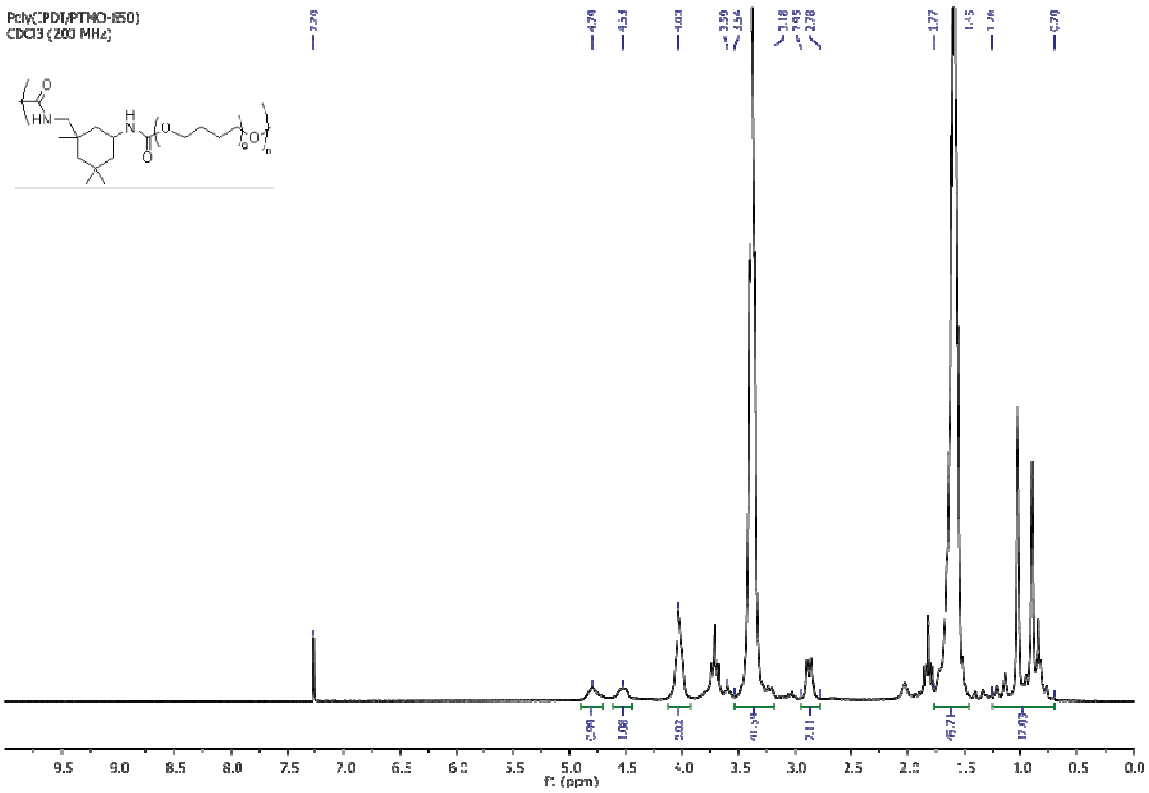
FT-IR spectrum of PU obtained using DBU-2BnNCO (**4b**) as catalyst

- **Comparison of PU obtained from Ia and IIa using MTBD-2BnNCO 2a and DBTDL as catalysts**

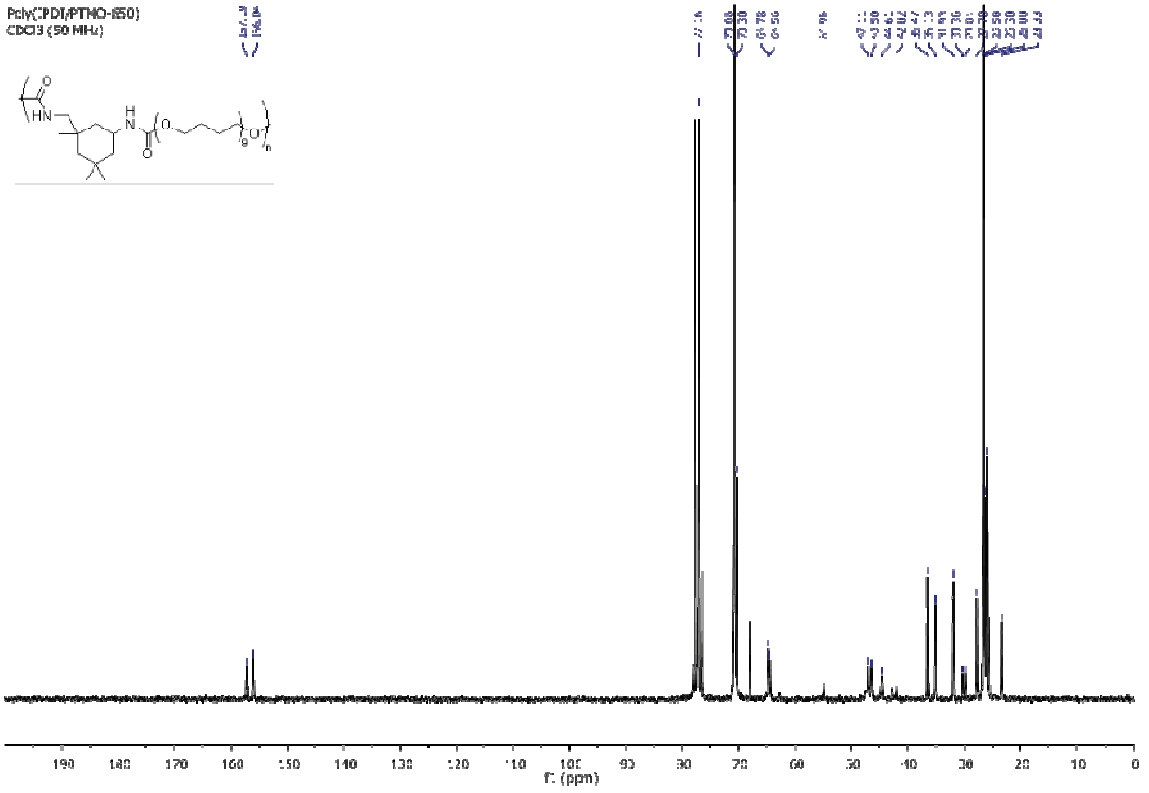


FT-IR spectra of PU (IPDI-PEG-600) obtained using MTBD-2BnNCO (**2a**) as catalyst (red) or using DBTDL as catalyst (blue)

- **NMR spectra of PU obtained from Ia and IIa using 2a as catalyst**

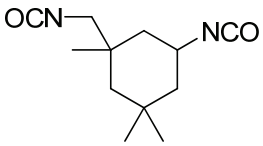


^{1}H NMR spectrum ($CDCl_3$, 200 MHz, 298 K) of PU obtained from **Ia** and **IIa** using **2a** as catalyst

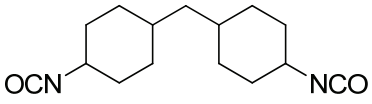


^{13}C NMR spectrum ($CDCl_3$, 50 MHz, 298 K) of PU obtained from **Ia** and **IIa** using **2a** as catalyst

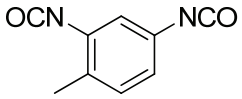
- **General procedure for the synthesis of PU from various monomers**



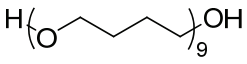
IPDI (**Ia**)



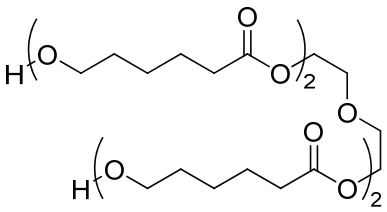
HMDI (**Ib**)



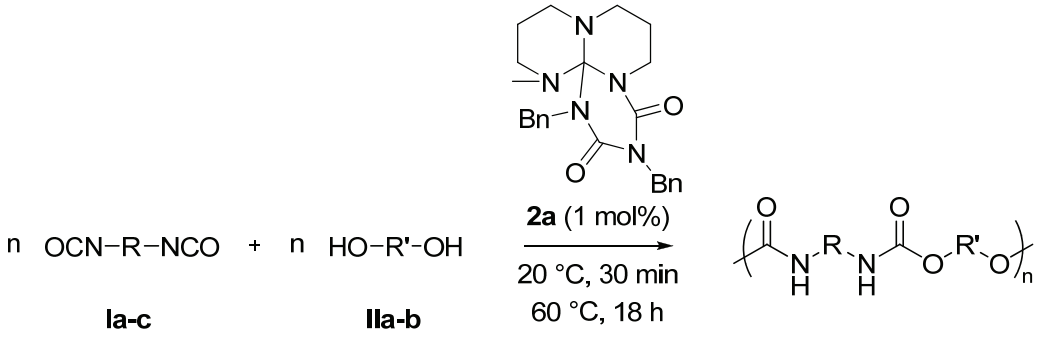
TDI (**Ic**)



PTMO-650 (**IIa**)

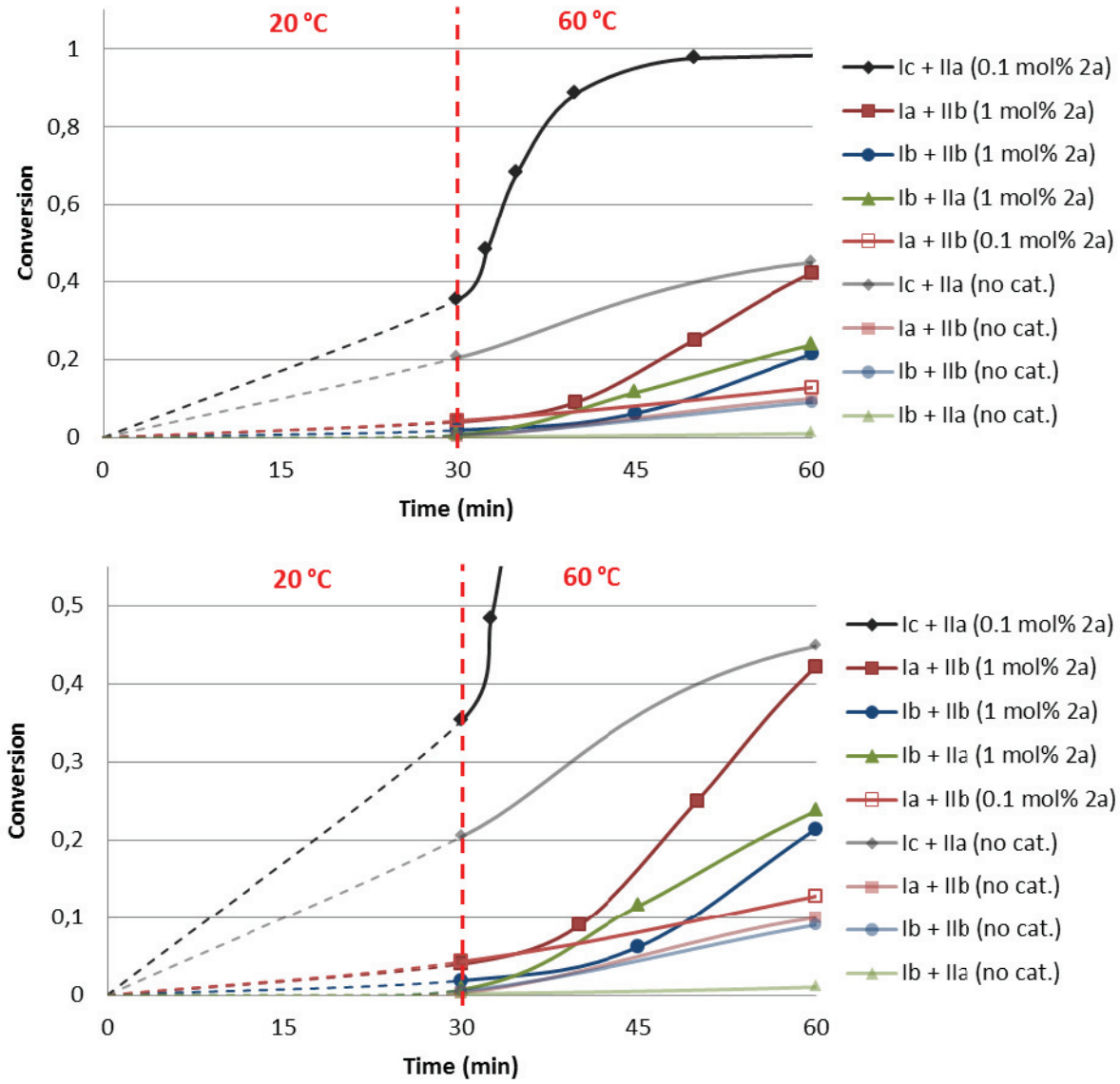


PCL-530 (**IIb**)



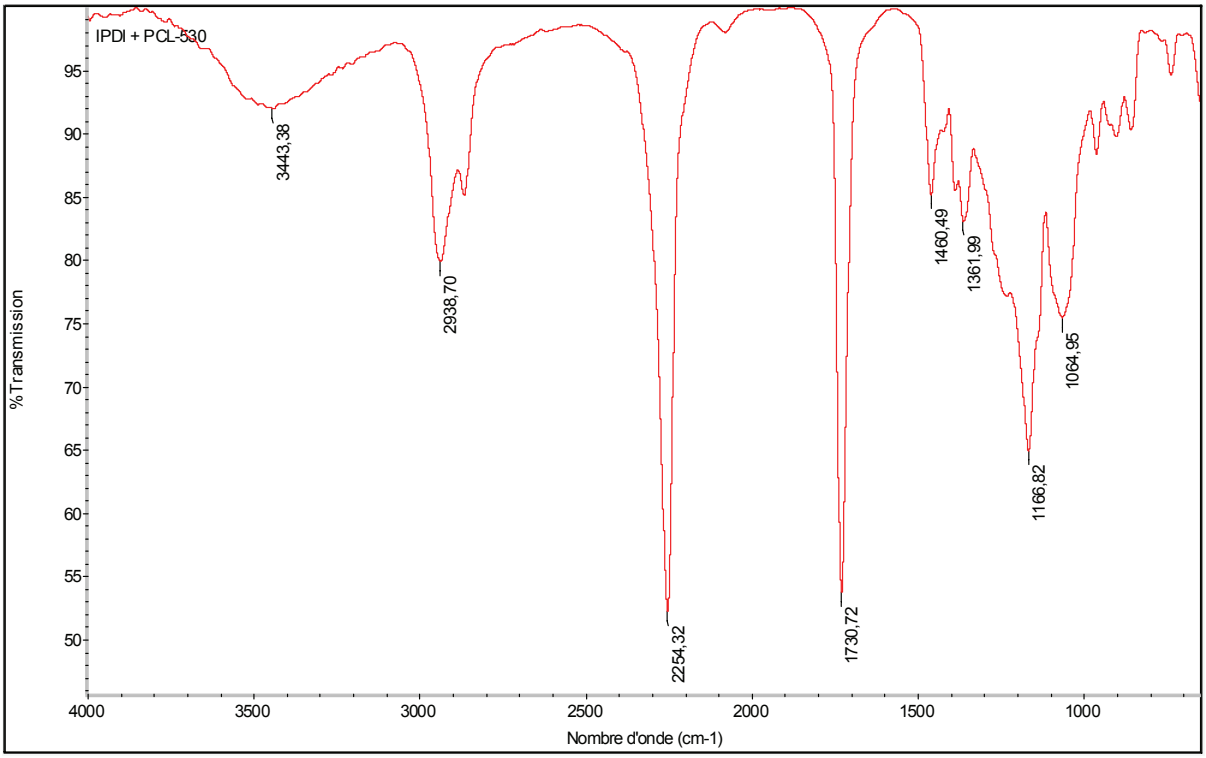
Diisocyanate **Ia-c** (3.78 mmol) was added to a stoichiometric amount of diol **IIa-b** (3.78 mmol) at room temperature (water bath at 20 °C). A solution of catalyst (75.5 µmol) in THF (0.5 mL) was added dropwise and the mixture was stirred 30 min at 20 °C. The flask was then placed in an oil bath at 60 °C and the mixture was stirred 18 h at this temperature. Aliquots were taken and IR spectra were recorded to monitor the time course of the reaction. An aliquot is taken at the end of the reaction and quenched with methanol for SEC analysis.

- **Zooms on the monitoring of the first hour conversion (*Figure 2*)**

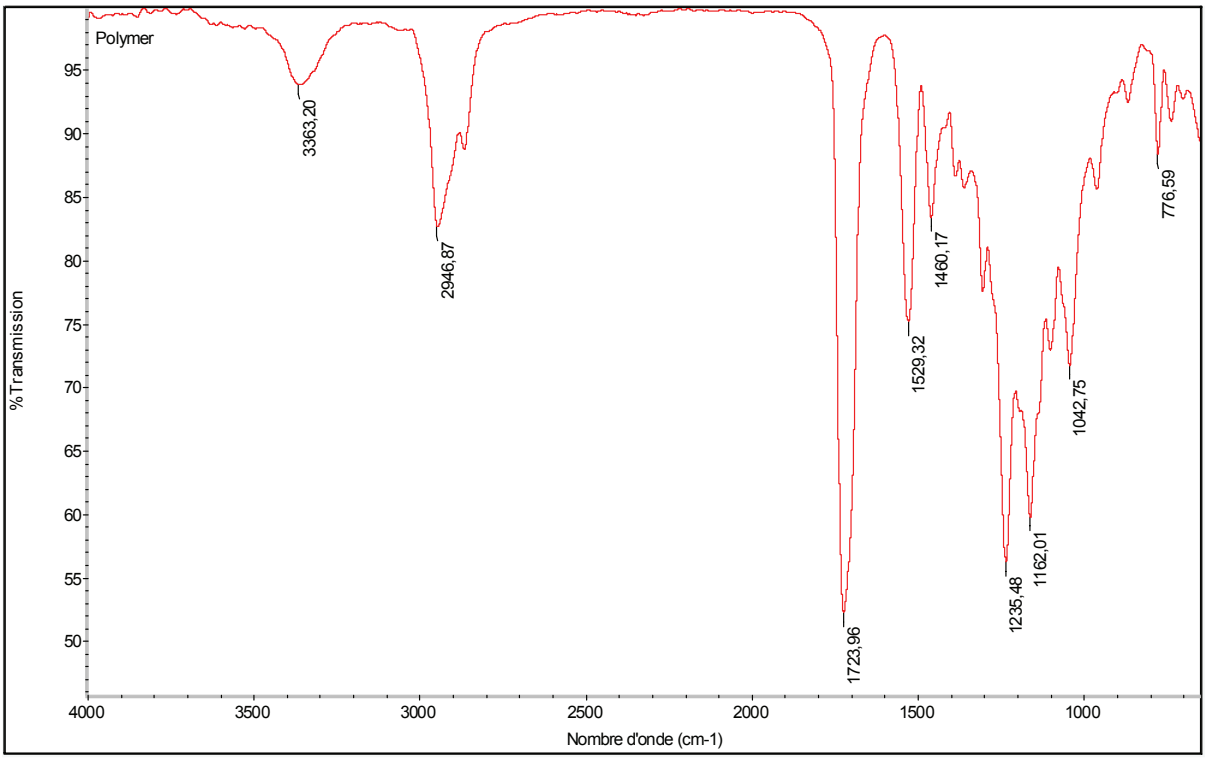


Delayed action catalysis during PU synthesis from diisocyanates **Ia-c** and diol **IIa-b**

➢ Synthesis of PU from IPDI **Ia** and PCL-530 **IIb**

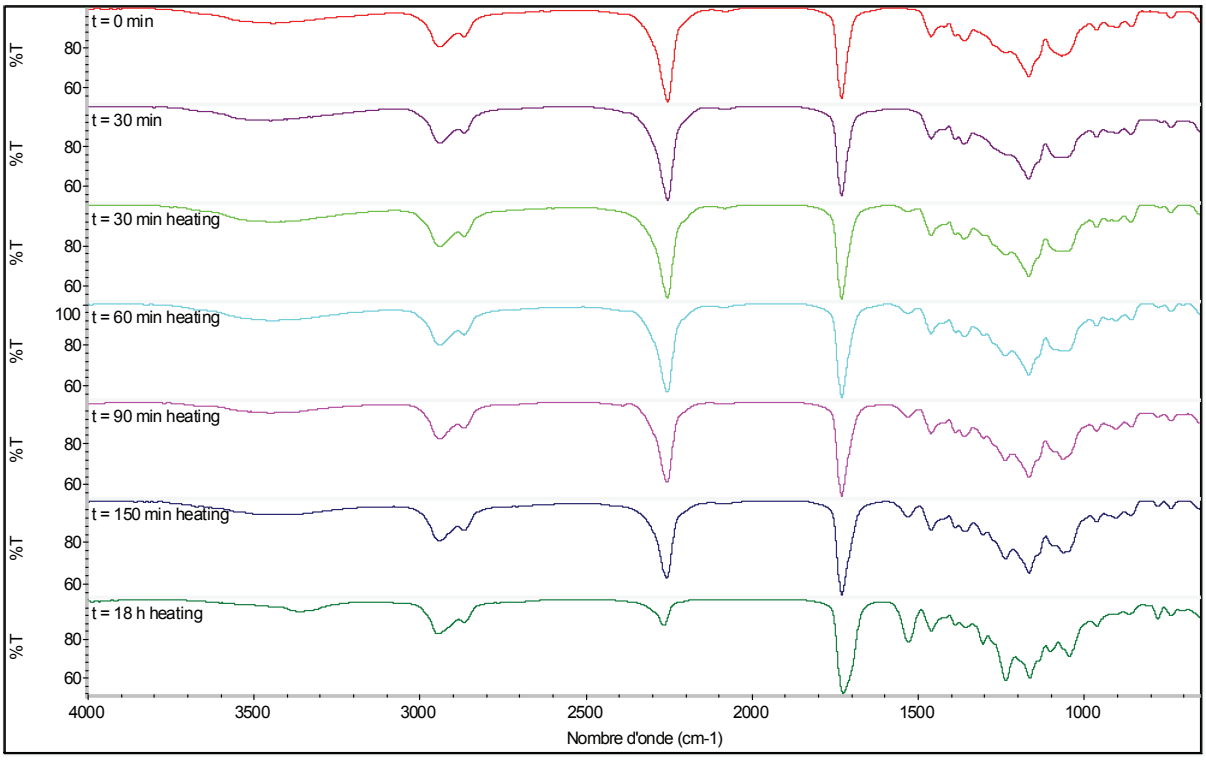


FT-IR spectrum of the starting mixture: IPDI **Ia** + PCL-530 **IIb**

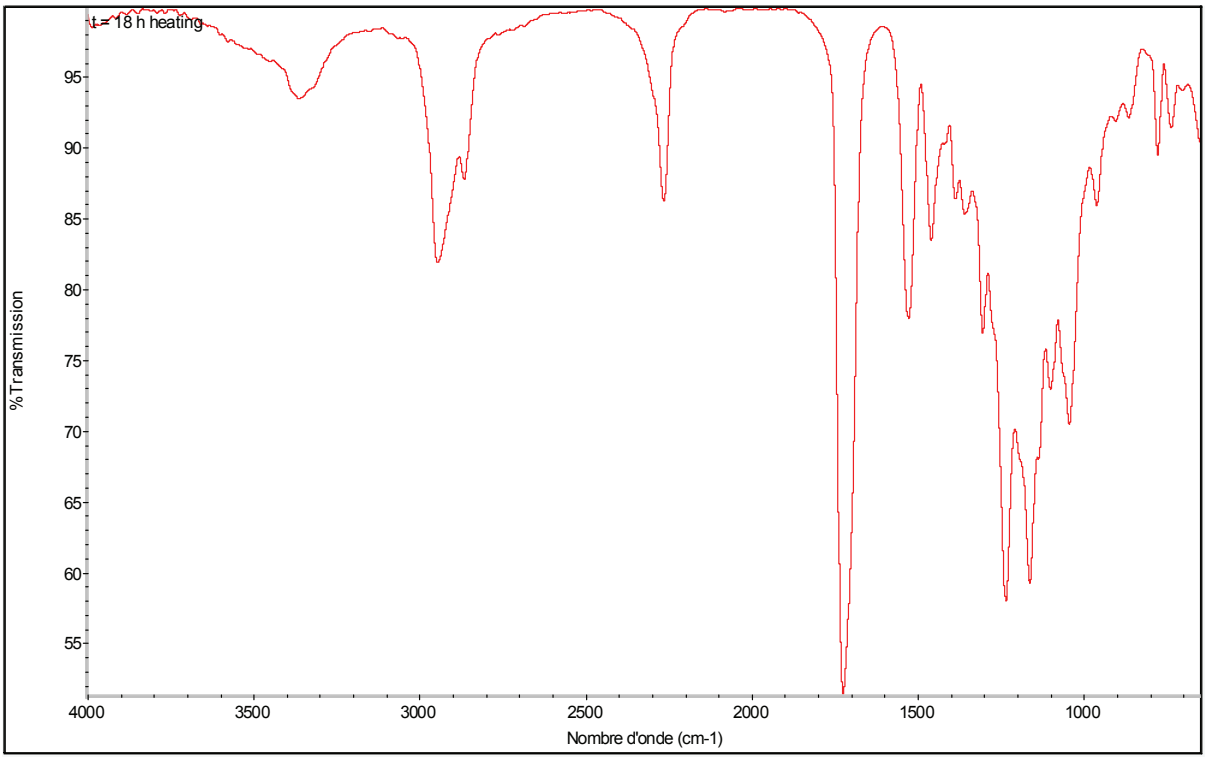


FT-IR spectrum of PU, obtained from IPDI **Ia** and PCL-530 **IIb**

➢ Synthesis of PU from **Ia** and **IIb** without catalyst

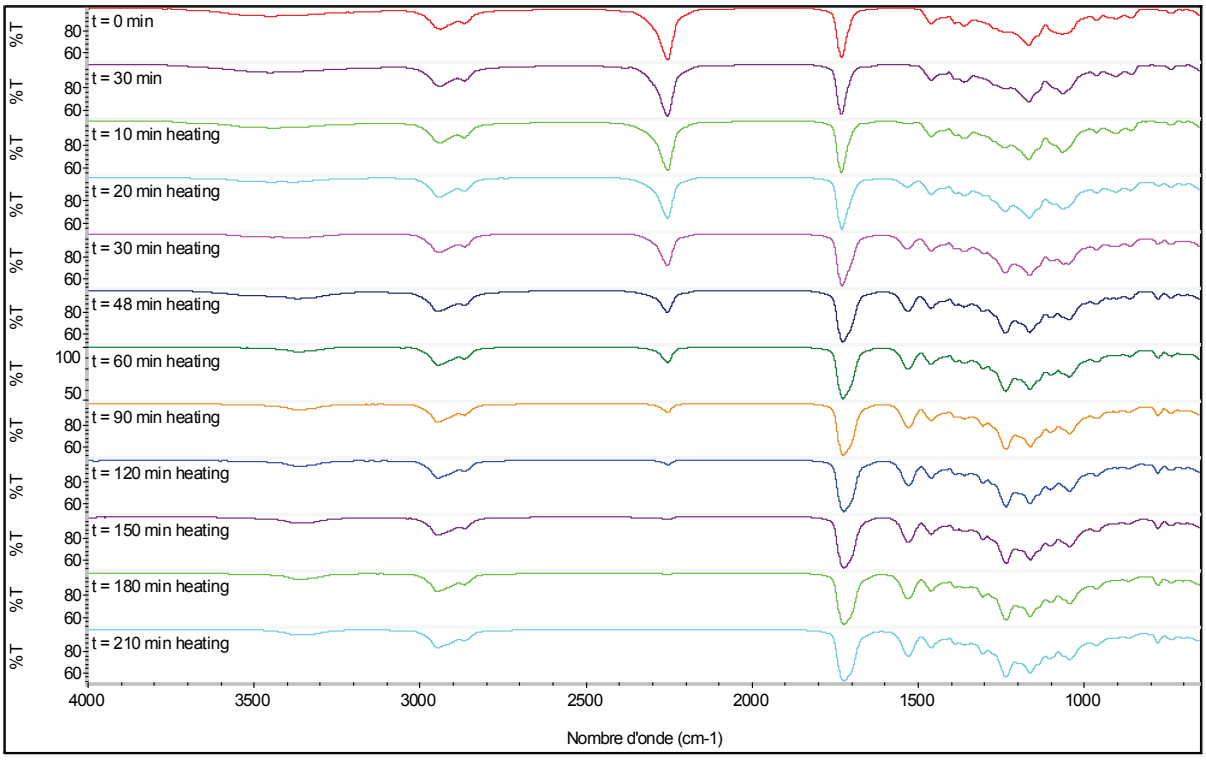


FT-IR spectra for the conversion monitoring (figure 2) without catalyst

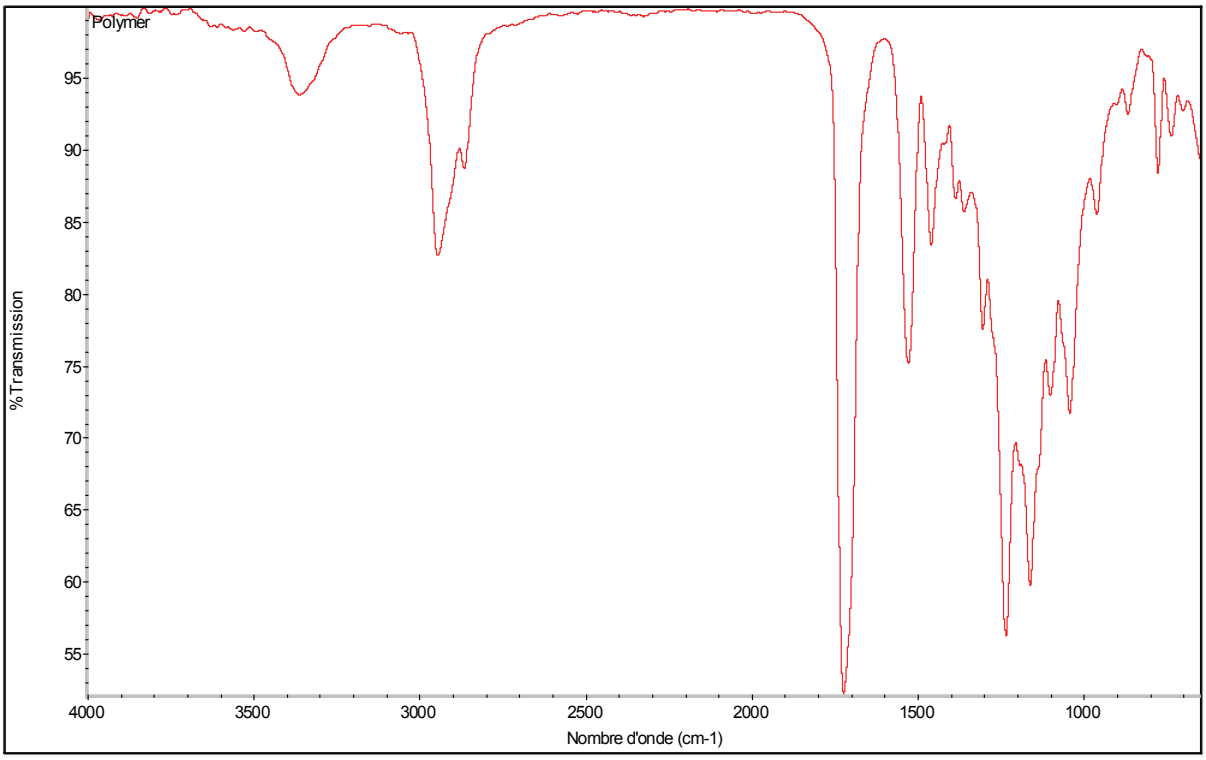


FT-IR spectrum of PU obtained without catalyst

➢ Synthesis of PU from **Ia** and **IIb** using MTBD-2BnNCO **2a** (1 mol%) as catalyst

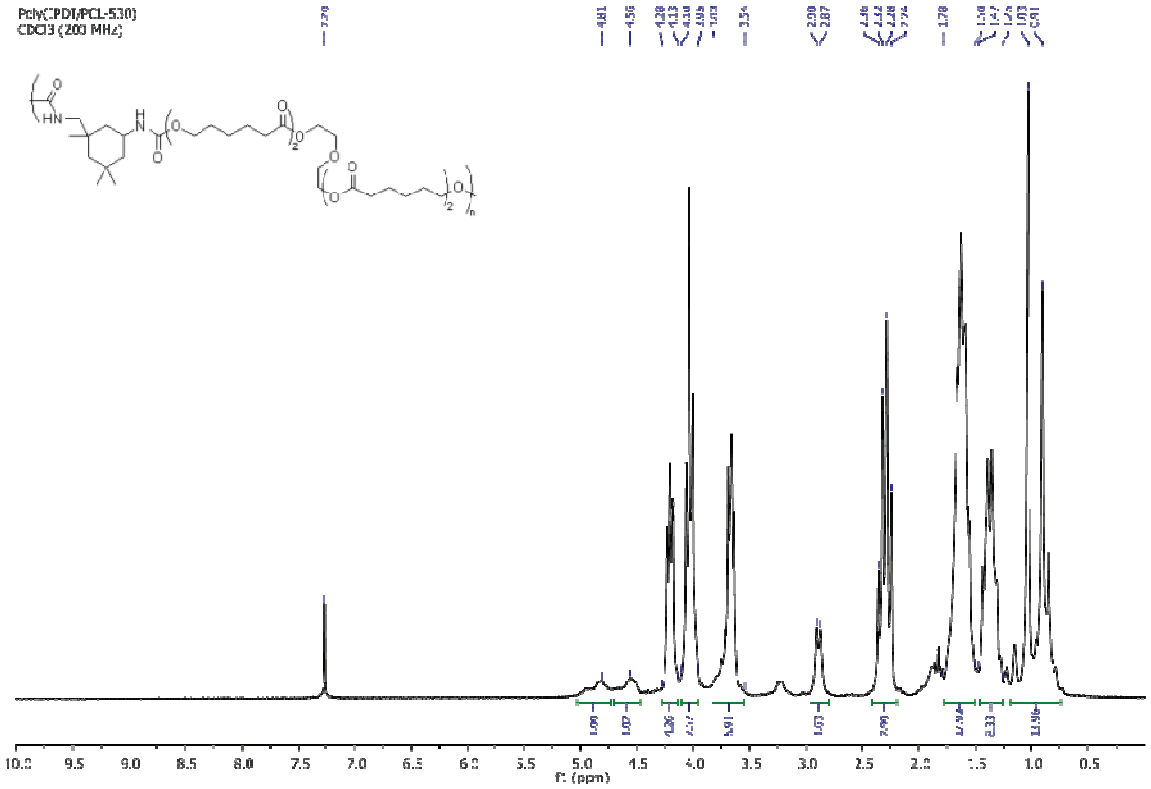


FT-IR spectra for the conversion monitoring (figure 2) using MTBD-2BnNCO (**2a**) as catalyst

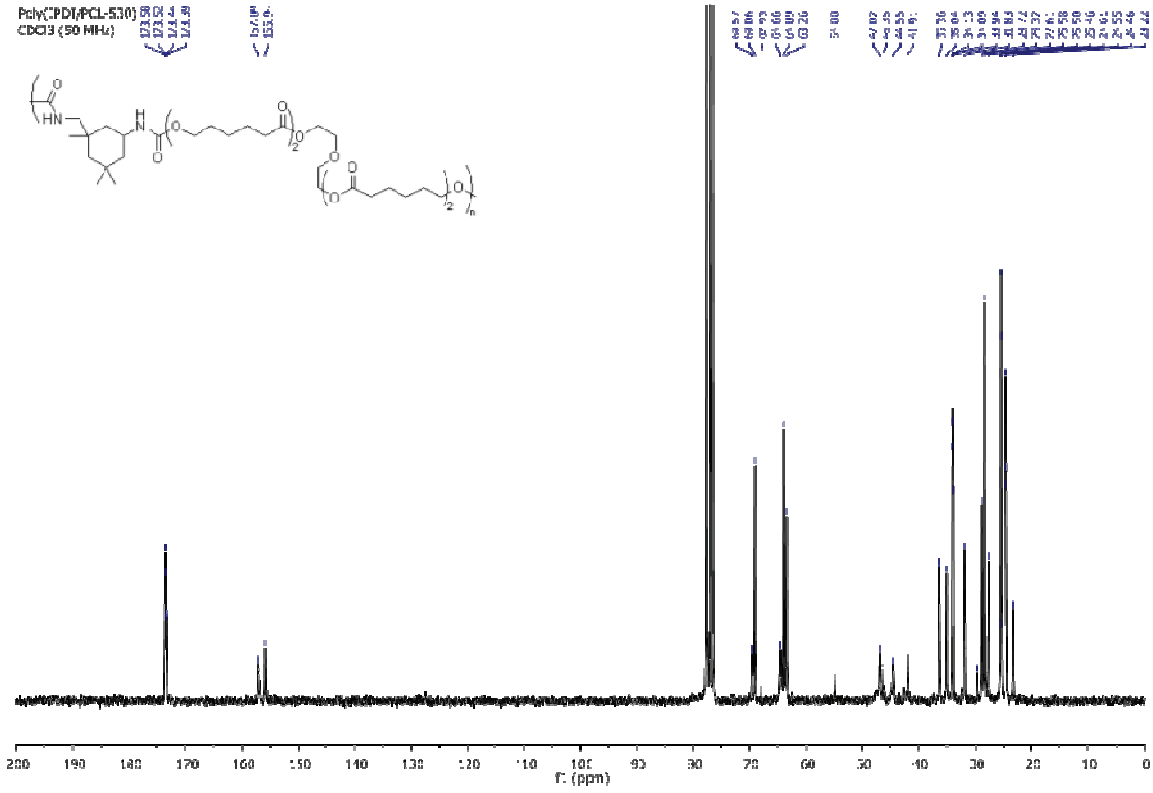


FT-IR spectrum of PU obtained using MTBD-2BnNCO (**2a**) as catalyst

- **NMR spectra of PU obtained from Ia and IIb using 2a as catalyst**

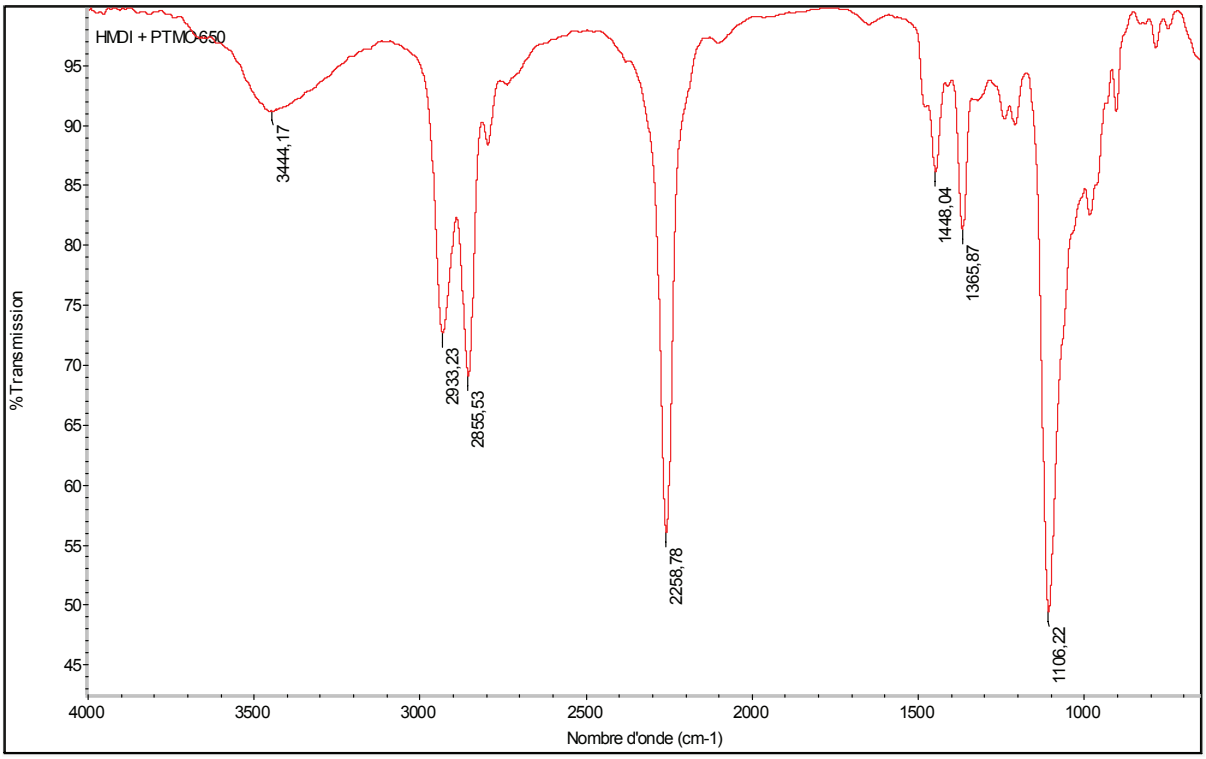


^{1}H NMR spectrum ($CDCl_3$, 200 MHz, 298 K) of PU obtained from **Ia** and **IIb** using **2a** as catalyst

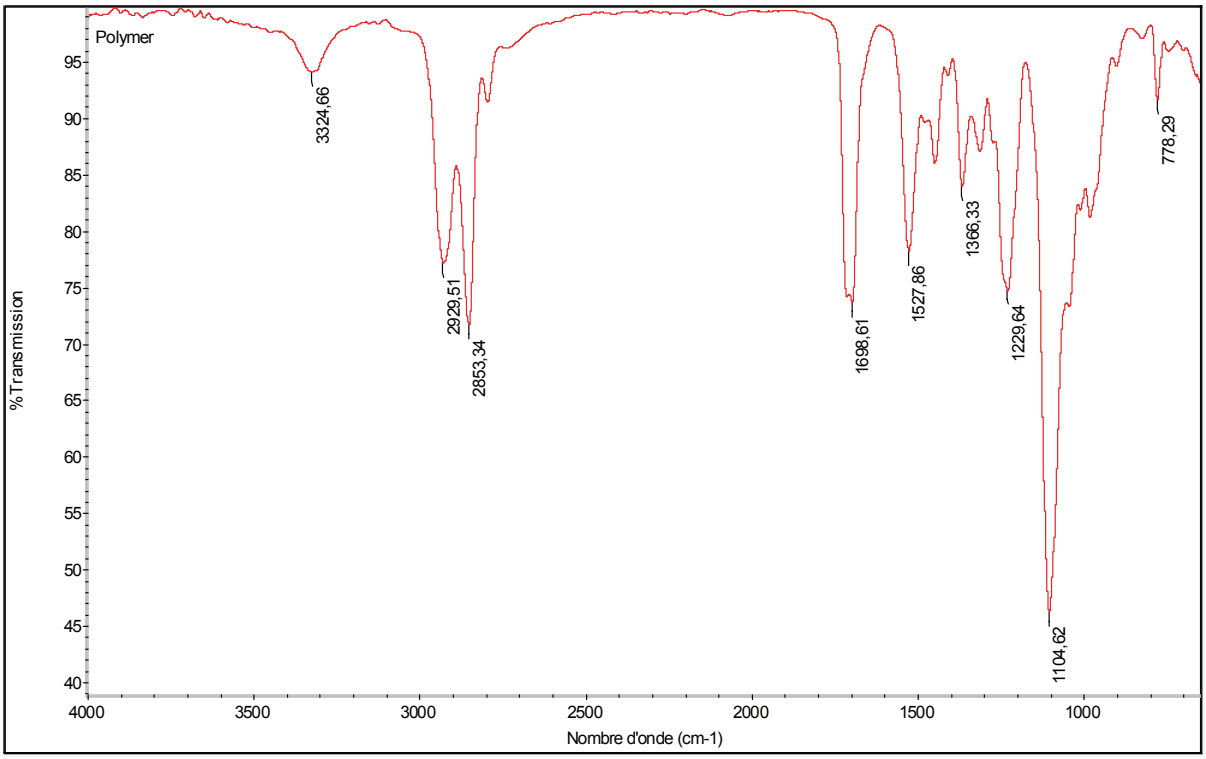


^{13}C NMR spectrum ($CDCl_3$, 50 MHz, 298 K) of PU obtained from **Ia** and **IIb** using **2a** as catalyst

➢ Synthesis of PU from HMDI (**Ib**) and PTMO-650 (**IIa**)

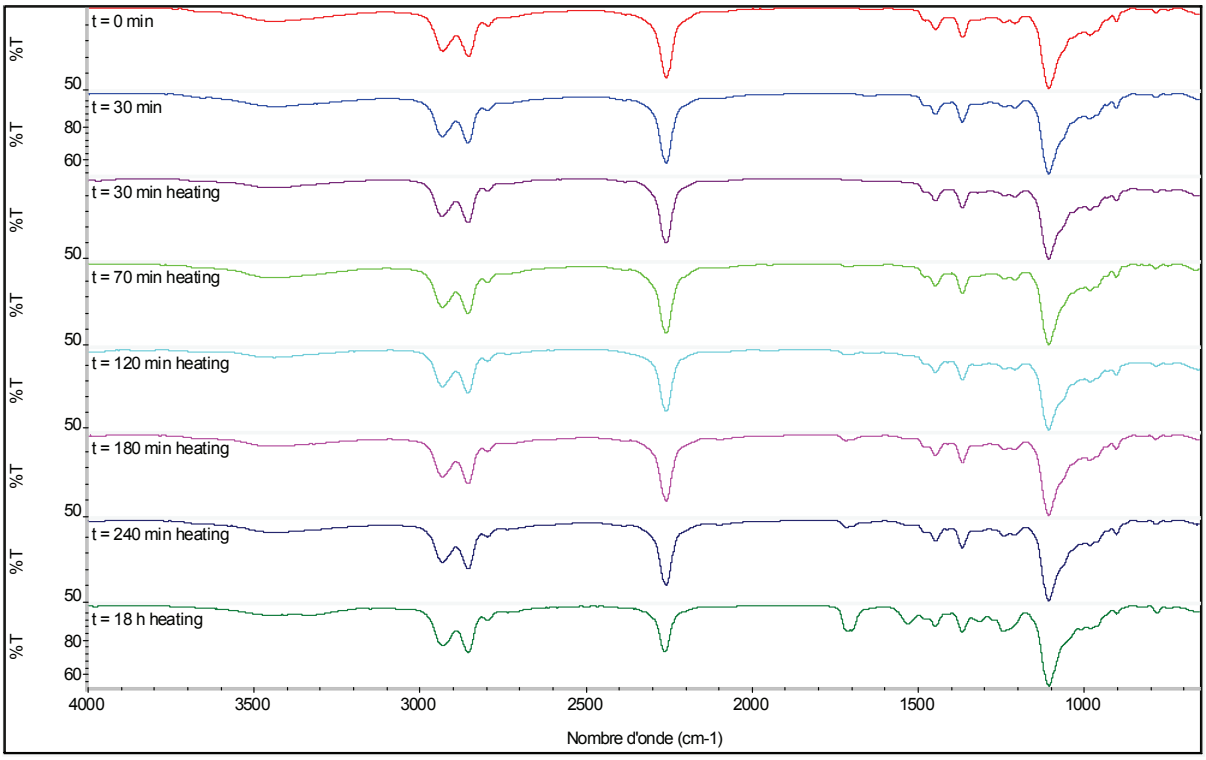


FT-IR spectrum of the starting mixture: HMDI **Ib** + PTMO-650 **IIa**

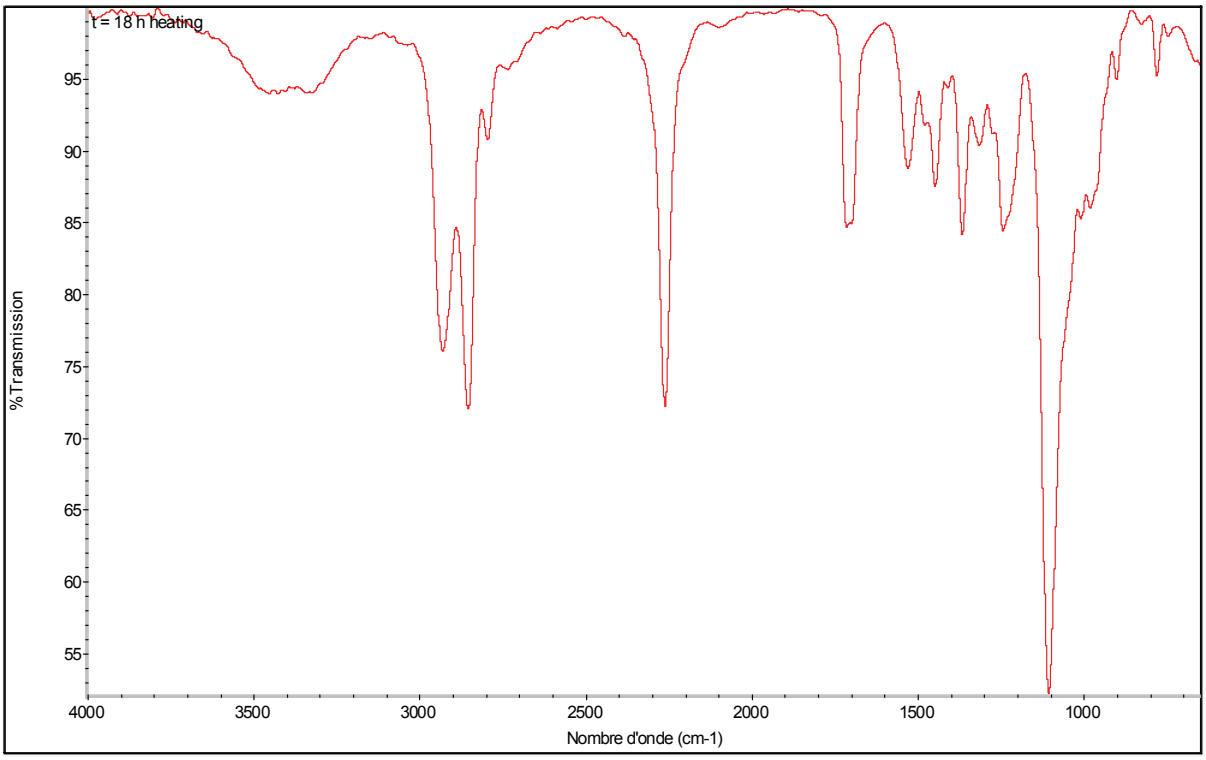


FT-IR spectrum of PU, obtained from HMDI **Ib** and PTMO-650 **IIa**

➢ Synthesis of PU from **Ib** and **IIa** without catalyst

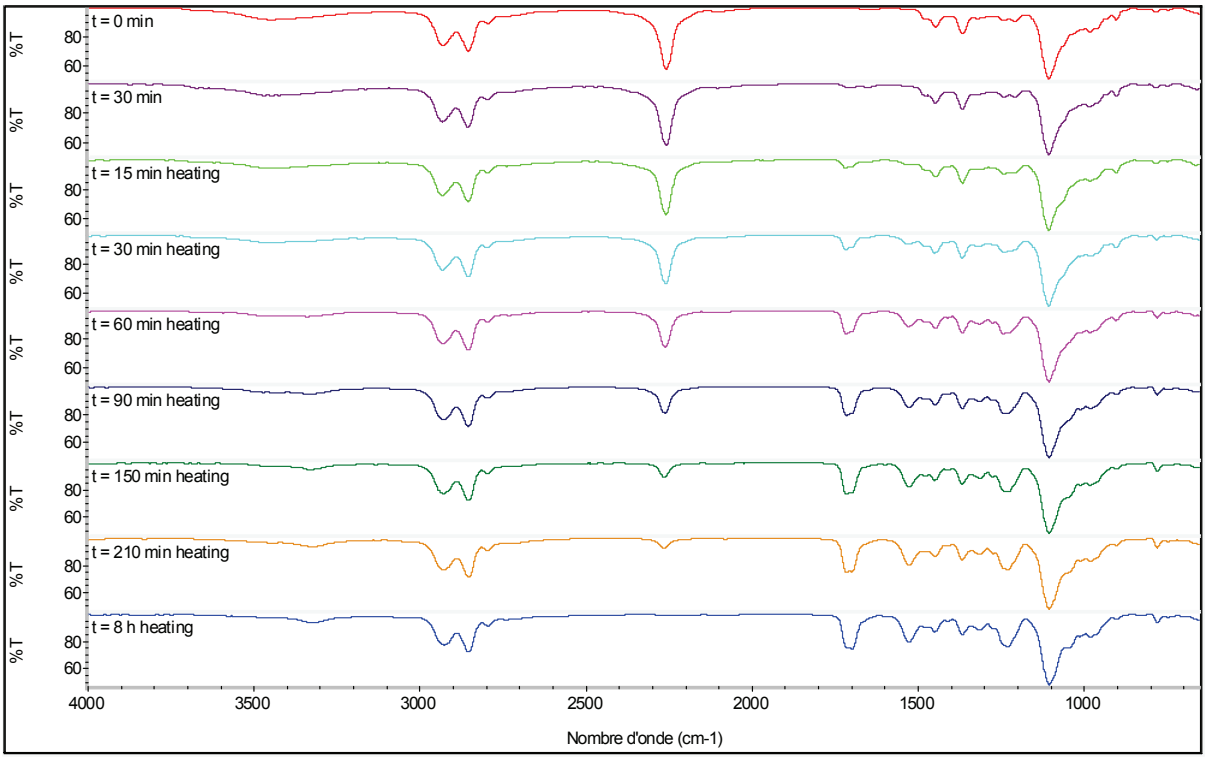


FT-IR spectra for the conversion monitoring (figure 2) without catalyst

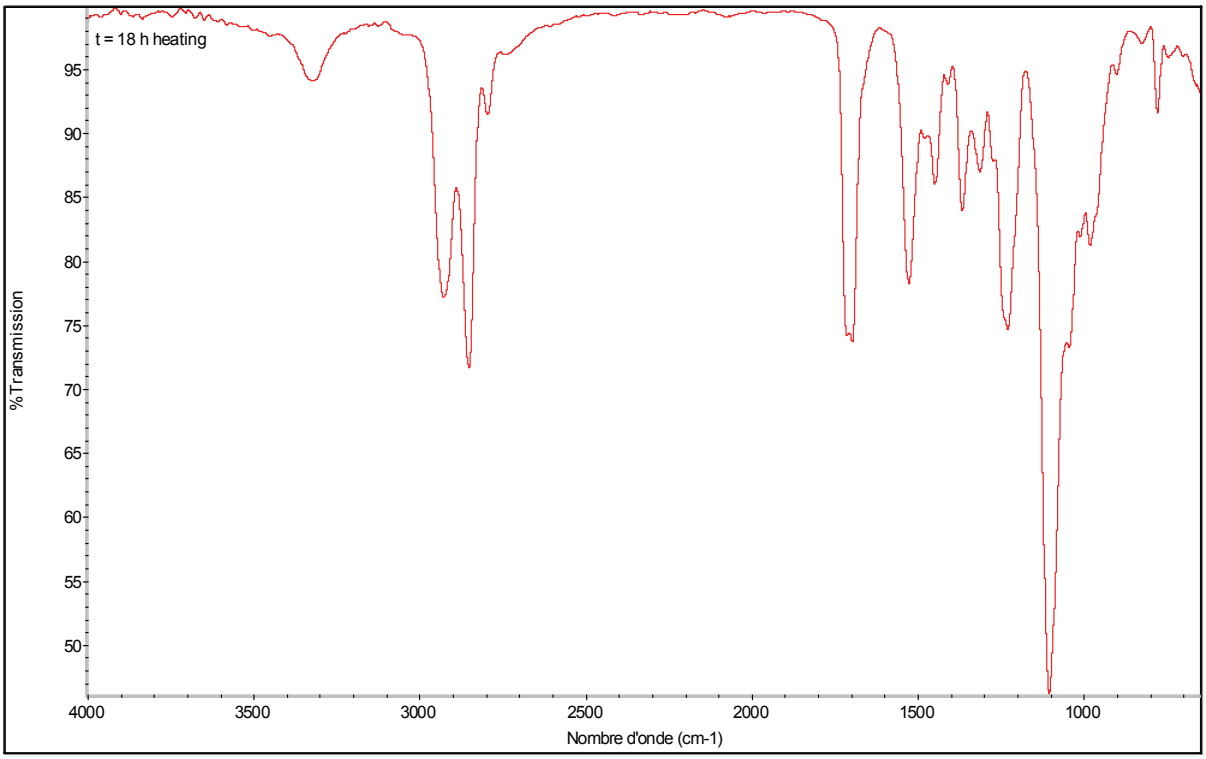


FT-IR spectrum of PU obtained without catalyst

➢ Synthesis of PU from **Ib** and **IIa** using MTBD-2BnNCO **2a** (1 mol%) as catalyst

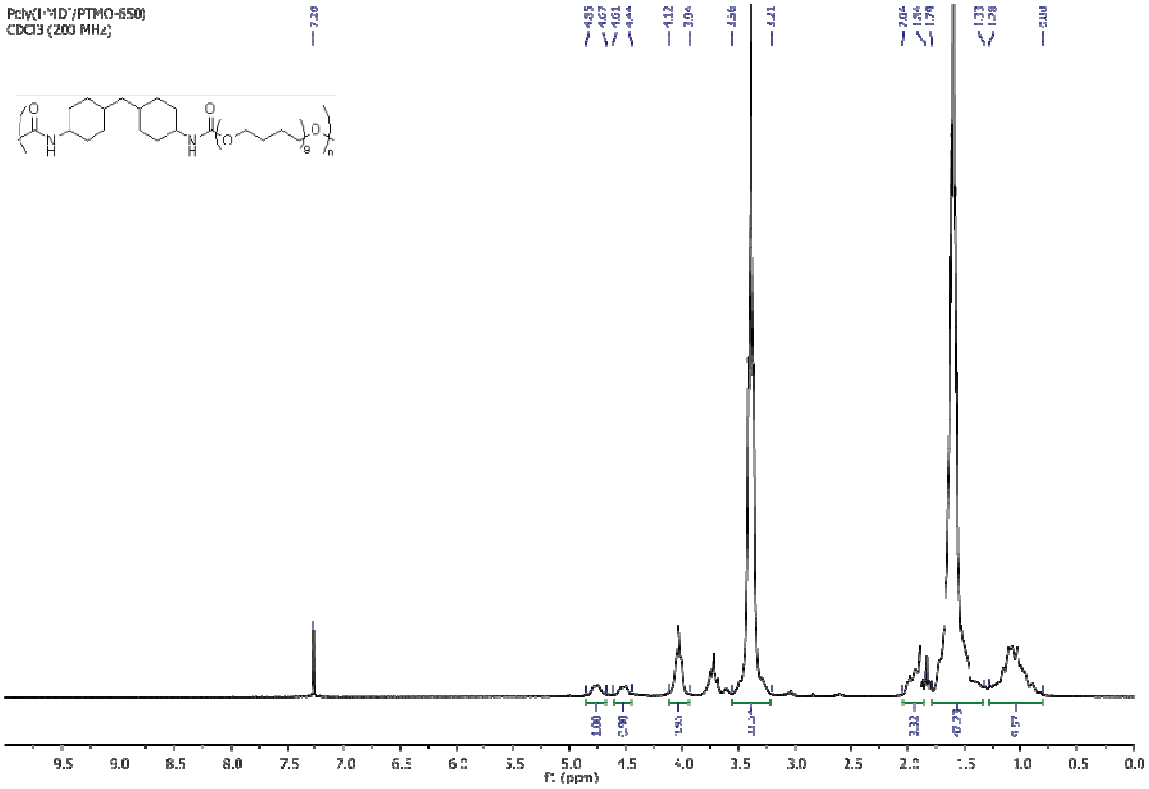


FT-IR spectra for the conversion monitoring (figure 2) using MTBD-2BnNCO (**2a**) as catalyst

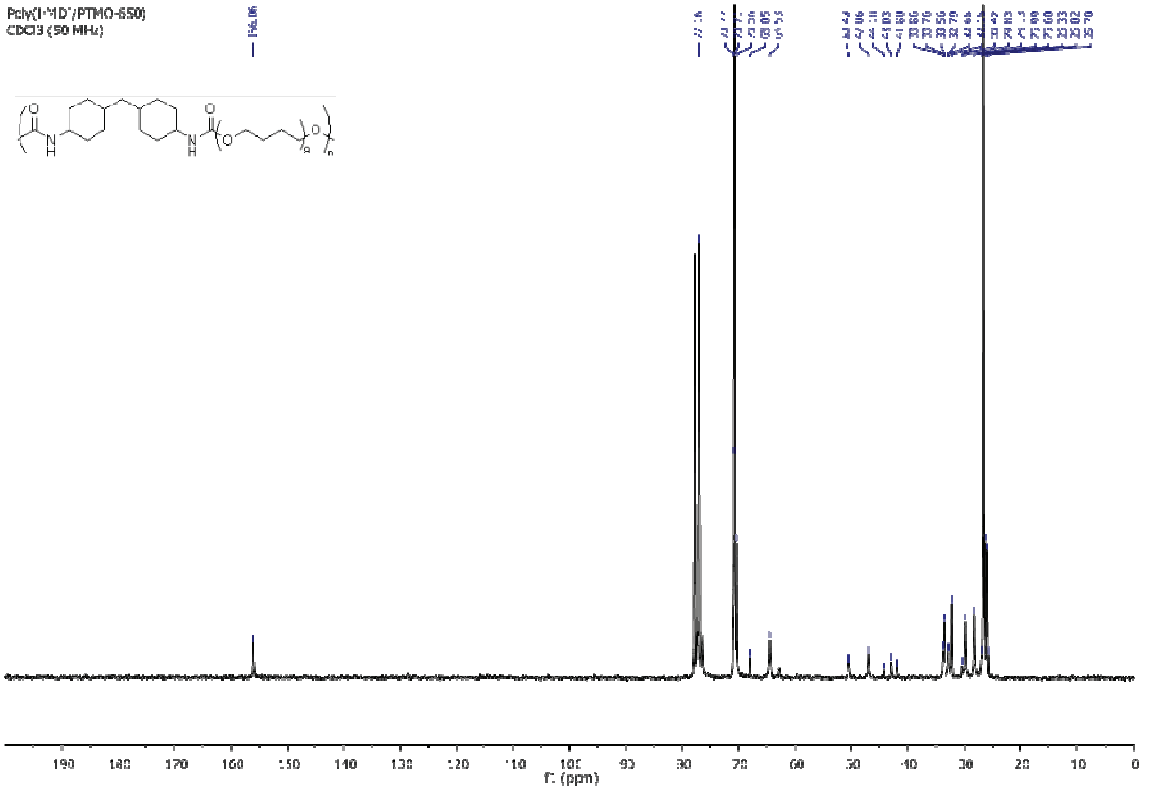


FT-IR spectrum of PU obtained using MTBD-2BnNCO (**2a**) as catalyst

- **RMN spectra of PU obtained from Ib and IIa using 2a as catalyst**

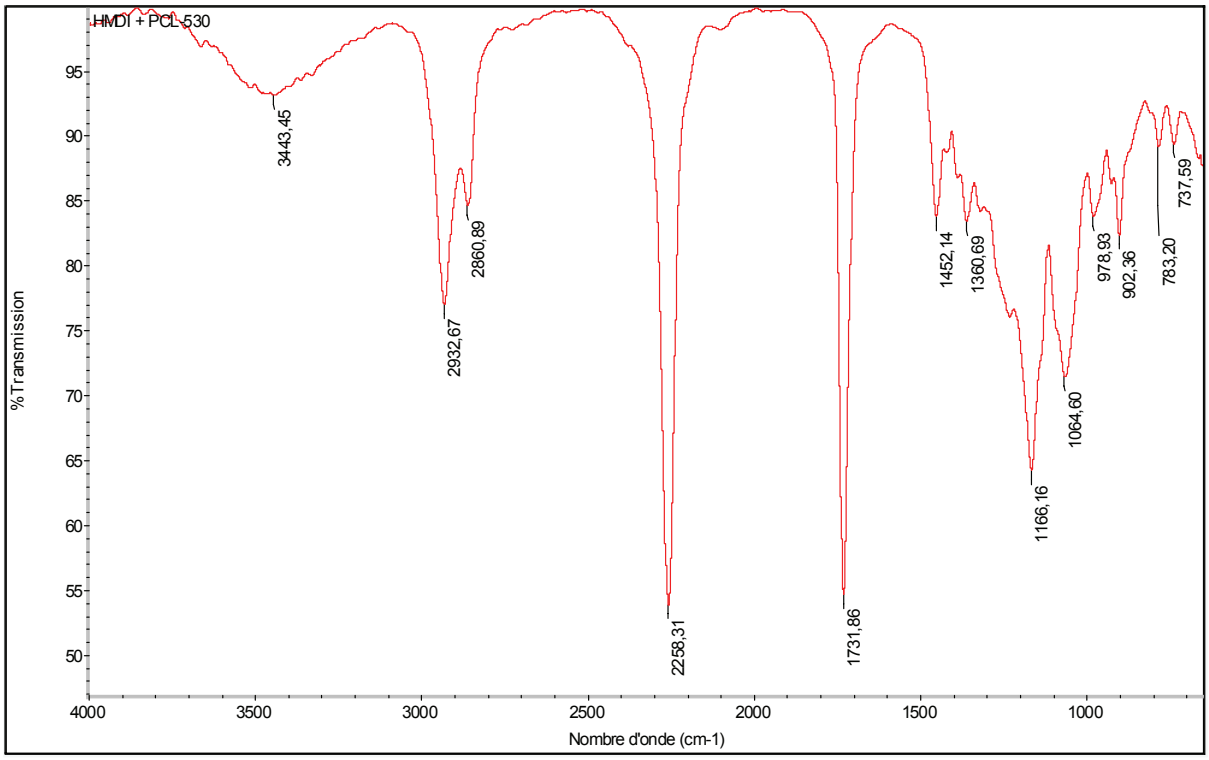


^{1}H NMR spectrum ($CDCl_3$, 200 MHz, 298 K) of PU obtained from **Ib** and **IIa** using **2a** as catalyst

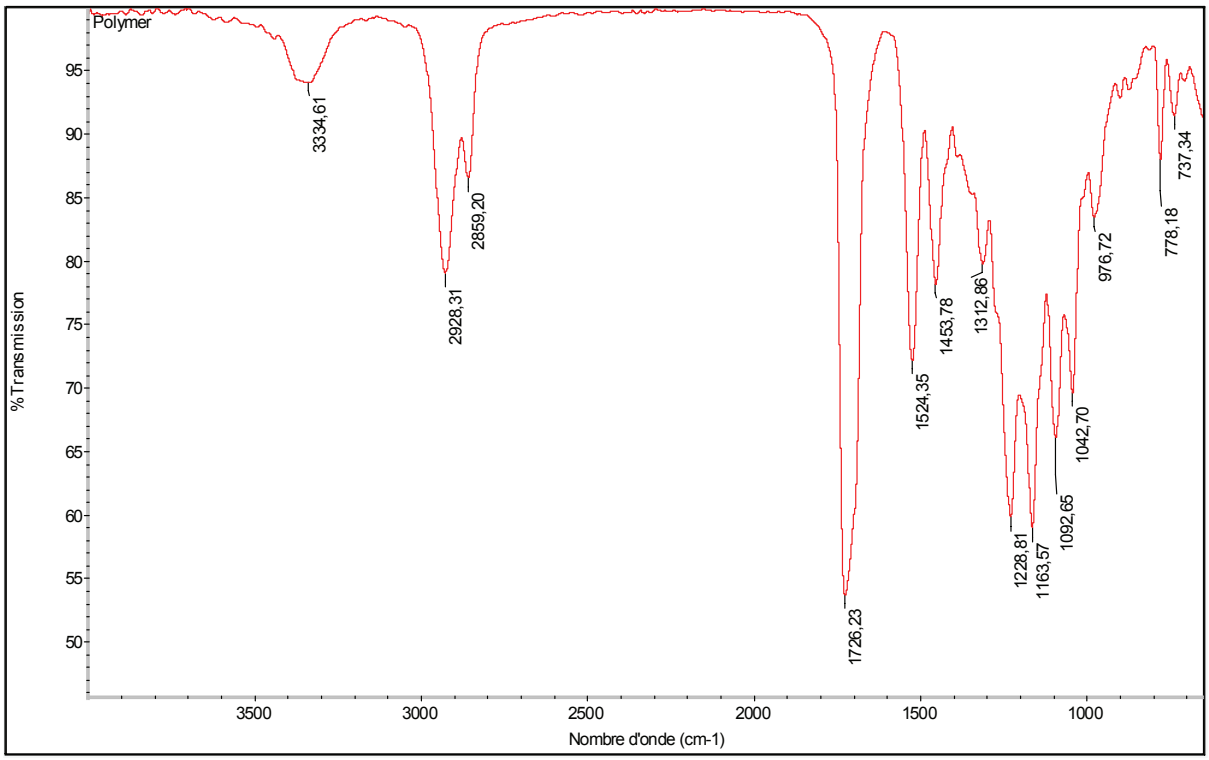


^{13}C NMR spectrum ($CDCl_3$, 50 MHz, 298 K) of PU obtained from **Ib** and **IIa** using **2a** as catalyst

➢ Synthesis of PU from HMDI (**Ib**) and PCL-530 (**IIb**)

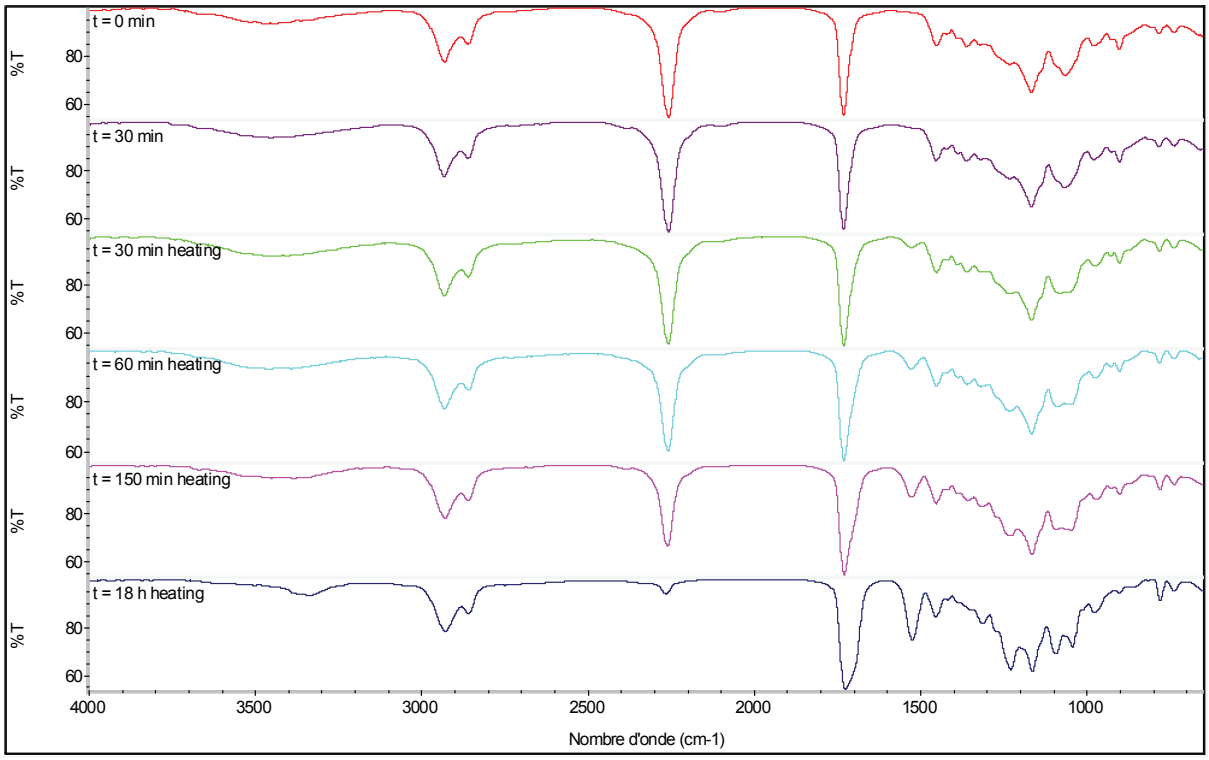


FT-IR spectrum of the starting mixture: HMDI **Ib** + PCL-530 **IIb**

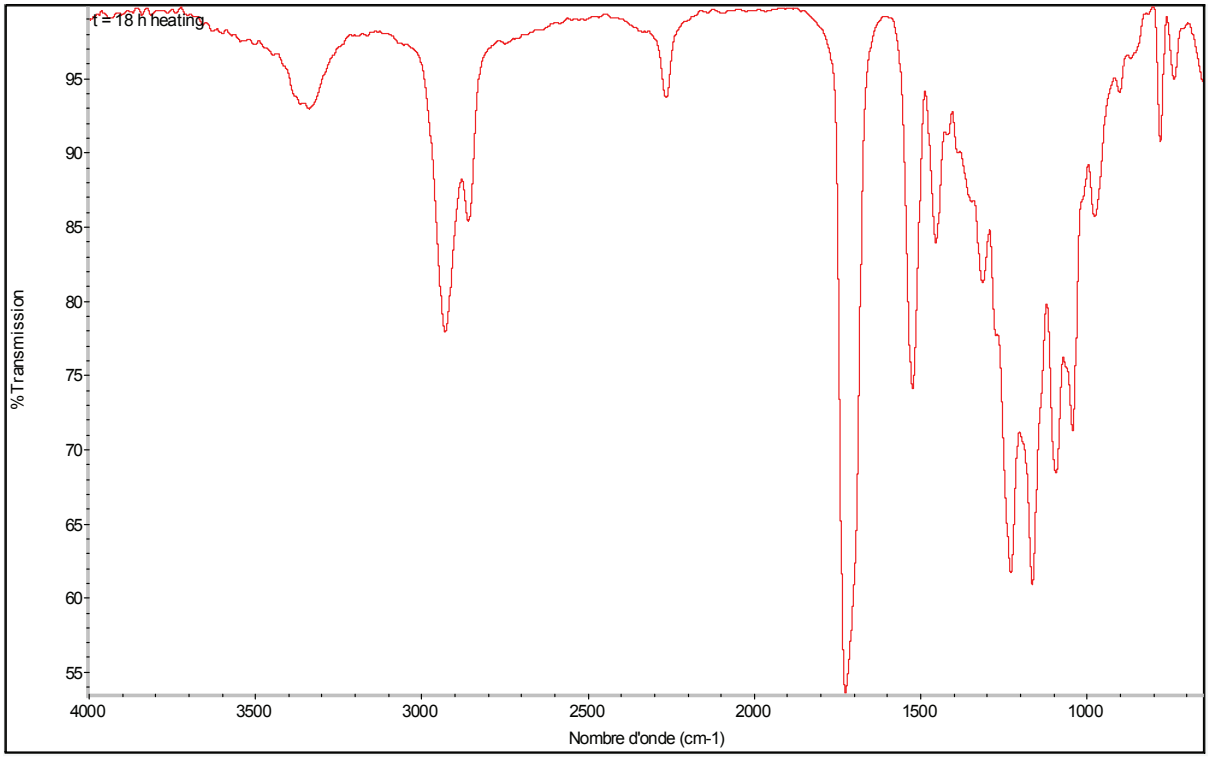


FT-IR spectrum of PU, obtained from HMDI **Ib** and PCL-530 **IIb**

➢ Synthesis of PU from **Ib** and **IIb** without catalyst

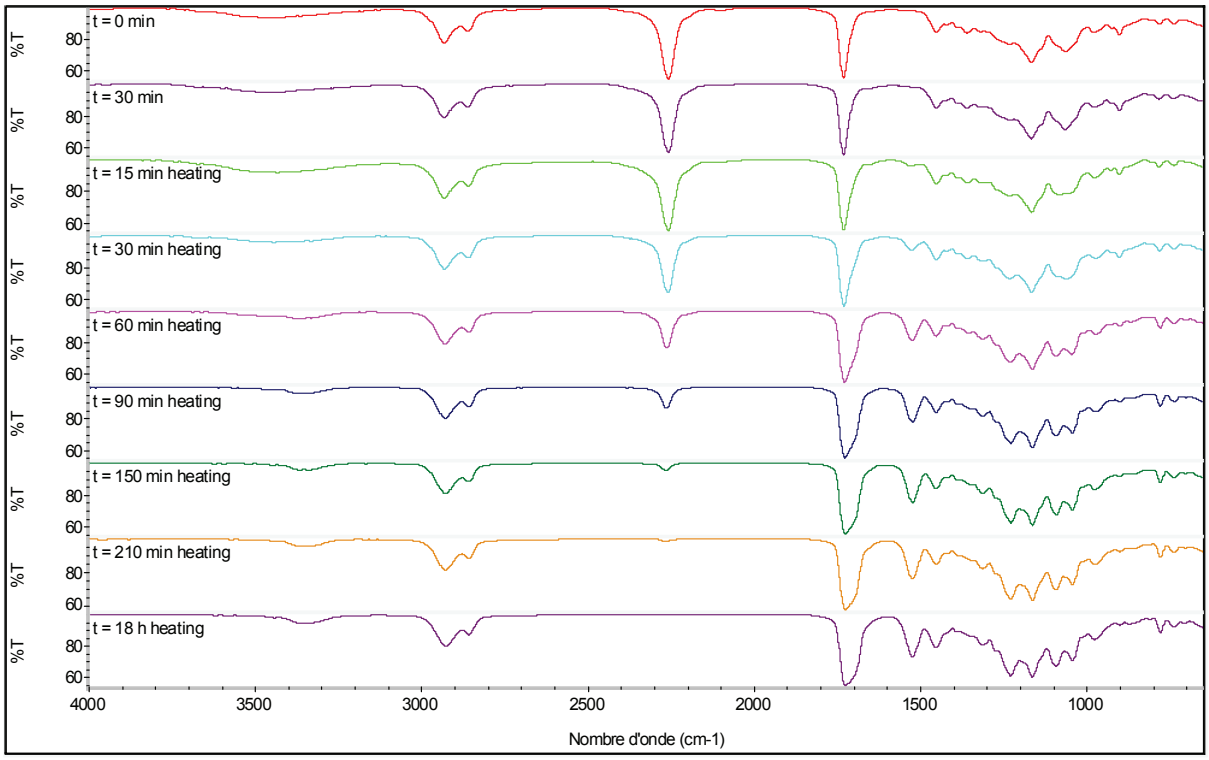


FT-IR spectra for the conversion monitoring (figure 2) without catalyst

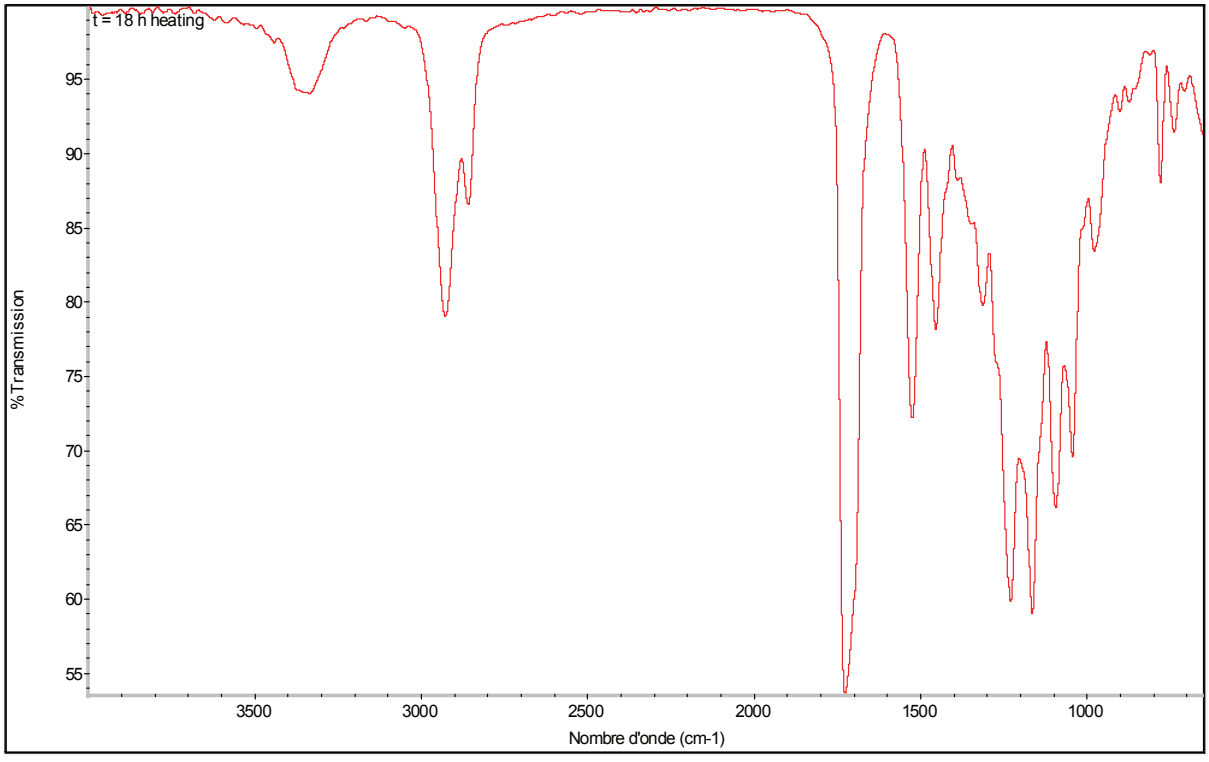


FT-IR spectrum of PU obtained without catalyst

➢ Synthesis of PU from **Ib** and **IIb** using MTBD-2BnNCO **2a** (1 mol%) as catalyst

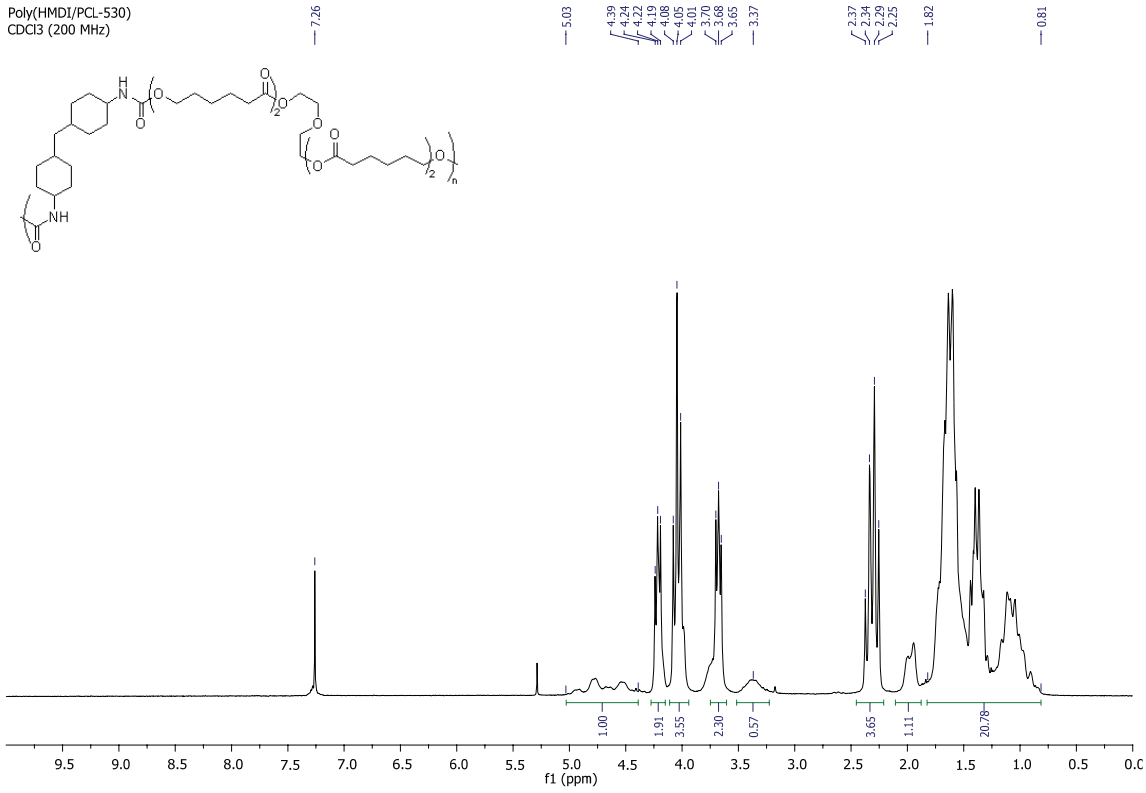


FT-IR spectra for the conversion monitoring (figure 2) using MTBD-2BnNCO (**2a**) as catalyst

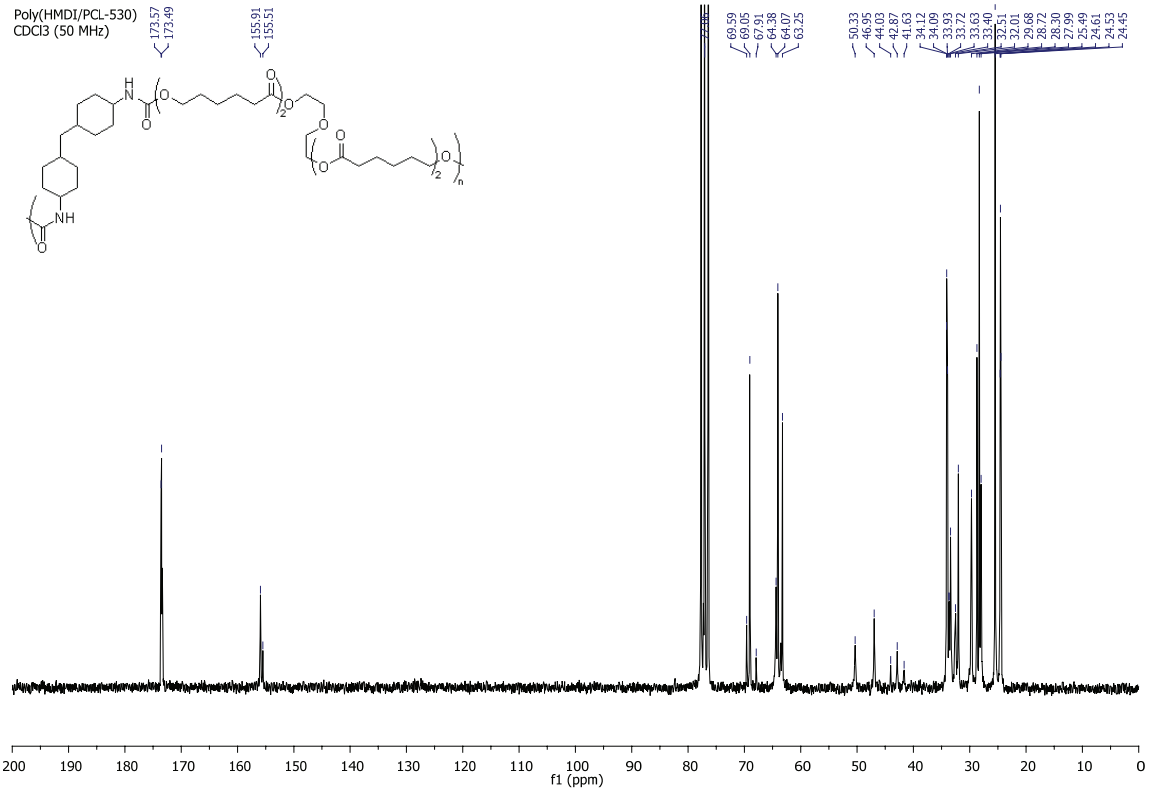


FT-IR spectrum of PU obtained using MTBD-2BnNCO (**2a**) as catalyst

RMN spectra of PU obtained from **Ib** and **IIb** using **2a** as catalyst

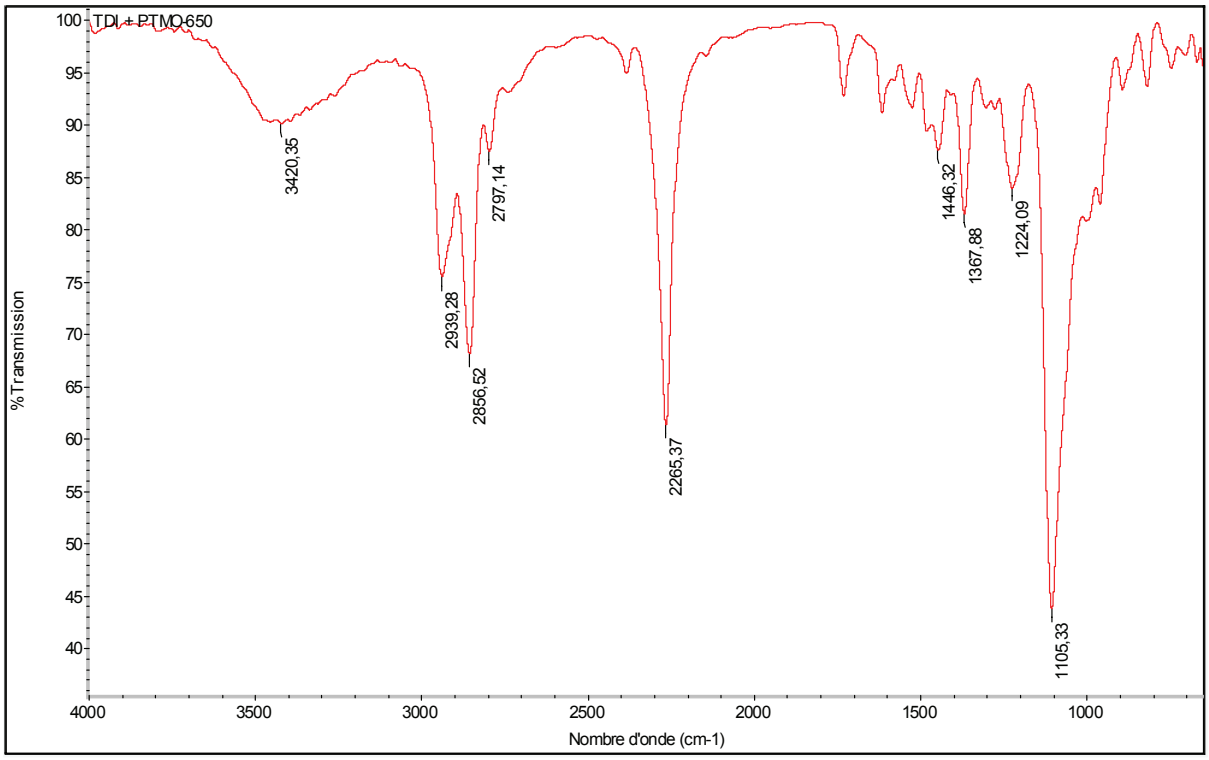


^{1}H NMR spectrum ($CDCl_3$, 200 MHz, 298 K) of PU obtained from **Ib** and **IIb** using **2a** as catalyst

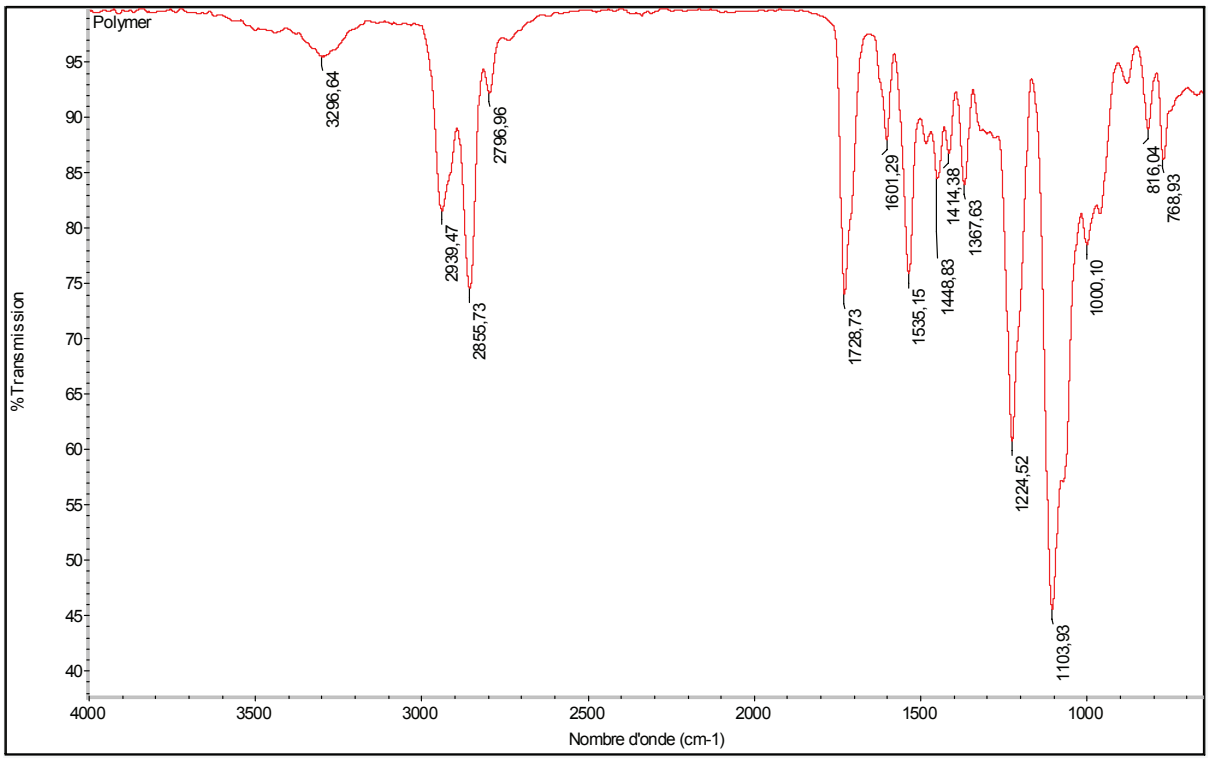


^{13}C NMR spectrum ($CDCl_3$, 50 MHz, 298 K) of PU obtained from **Ib** and **IIb** using **2a** as catalyst

➢ Synthesis of PU from TDI (**Ic**) and PTMO-650 (**IIa**)

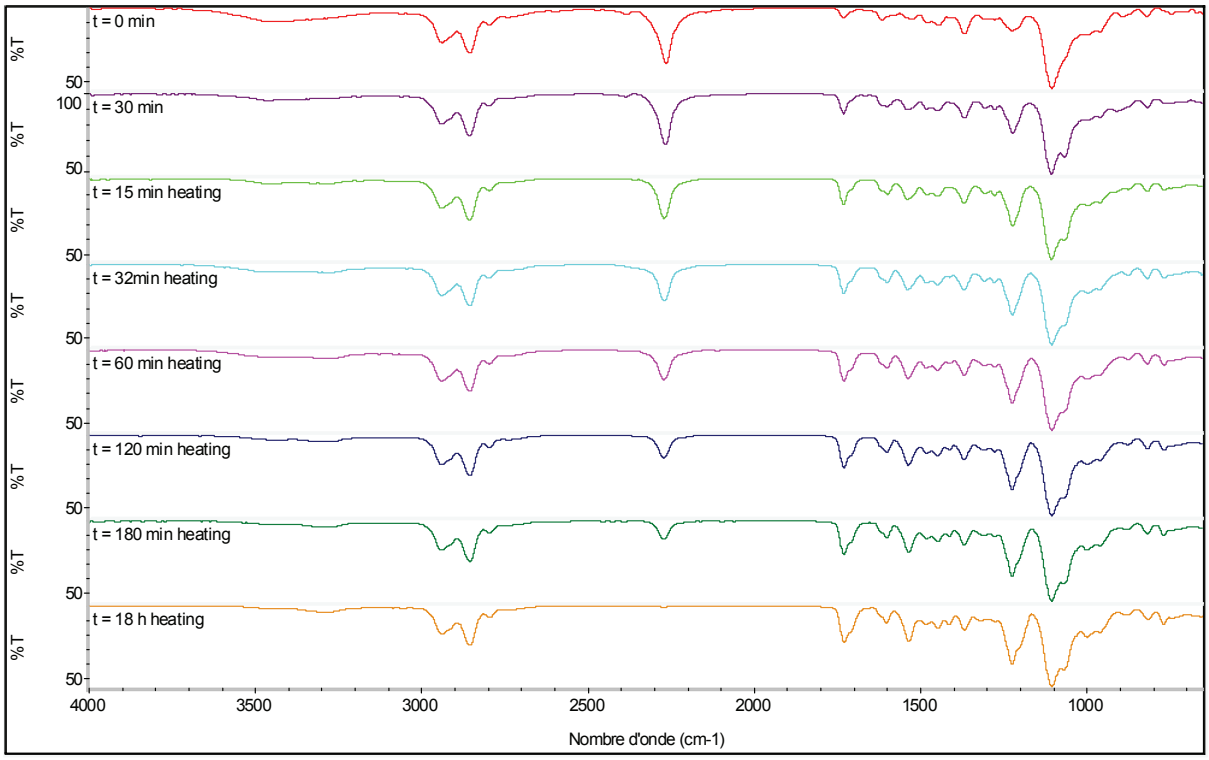


FT-IR spectrum of the starting mixture: TDI **Ic** + PTMO-650 **IIa**

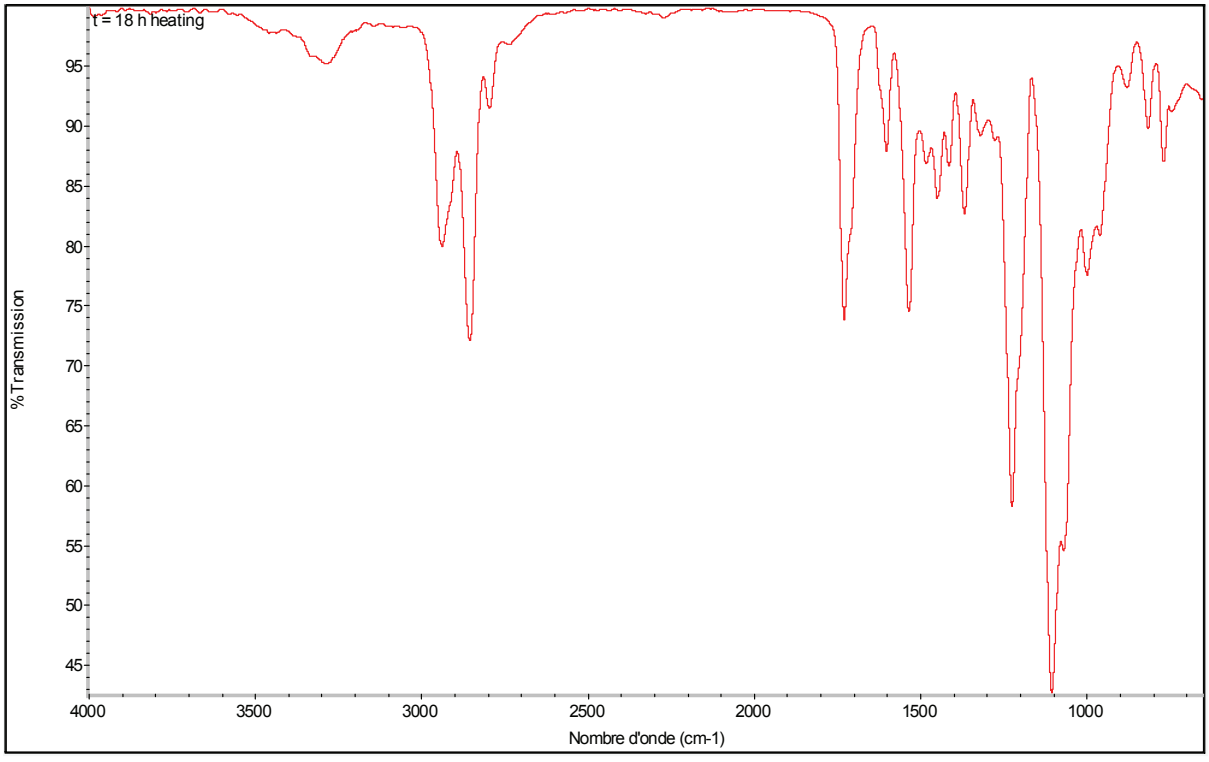


FT-IR spectrum of PU, obtained from TDI **Ic** and PTMO-650 **IIa**

➢ Synthesis of PU from **Ic** and **IIa** without catalyst

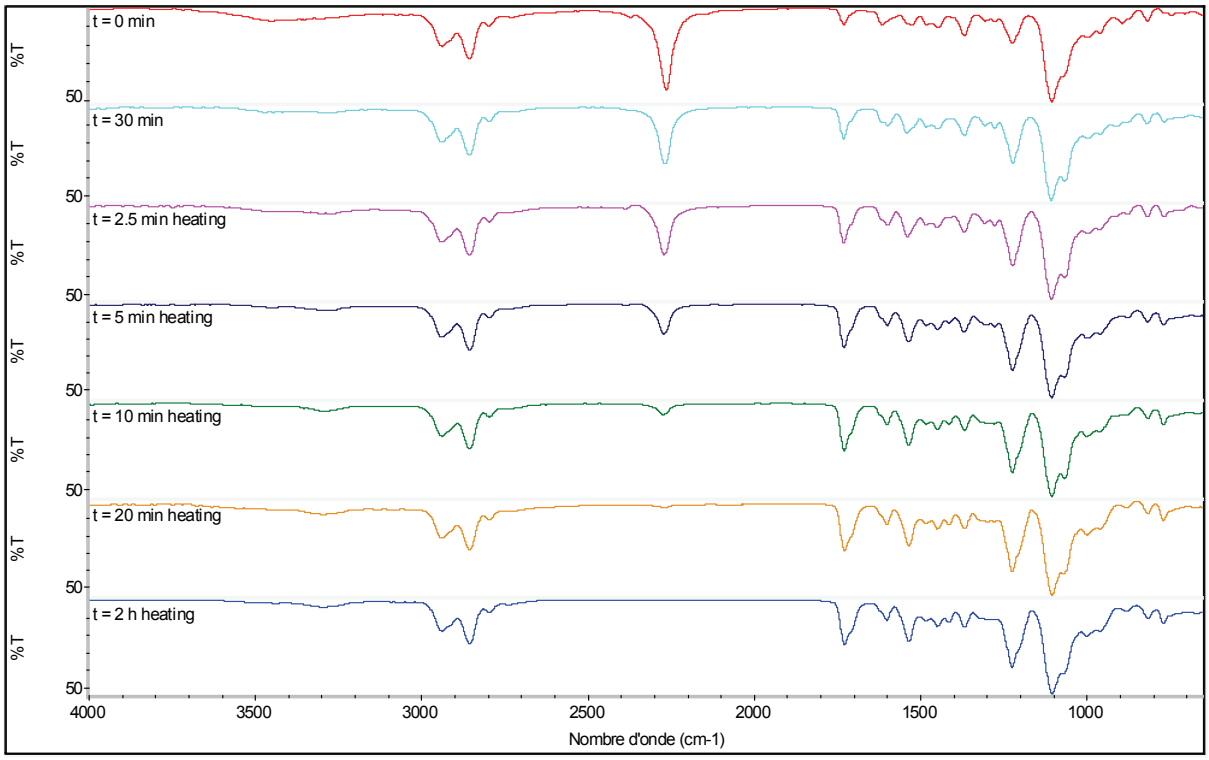


FT-IR spectra for the conversion monitoring (figure 2) without catalyst

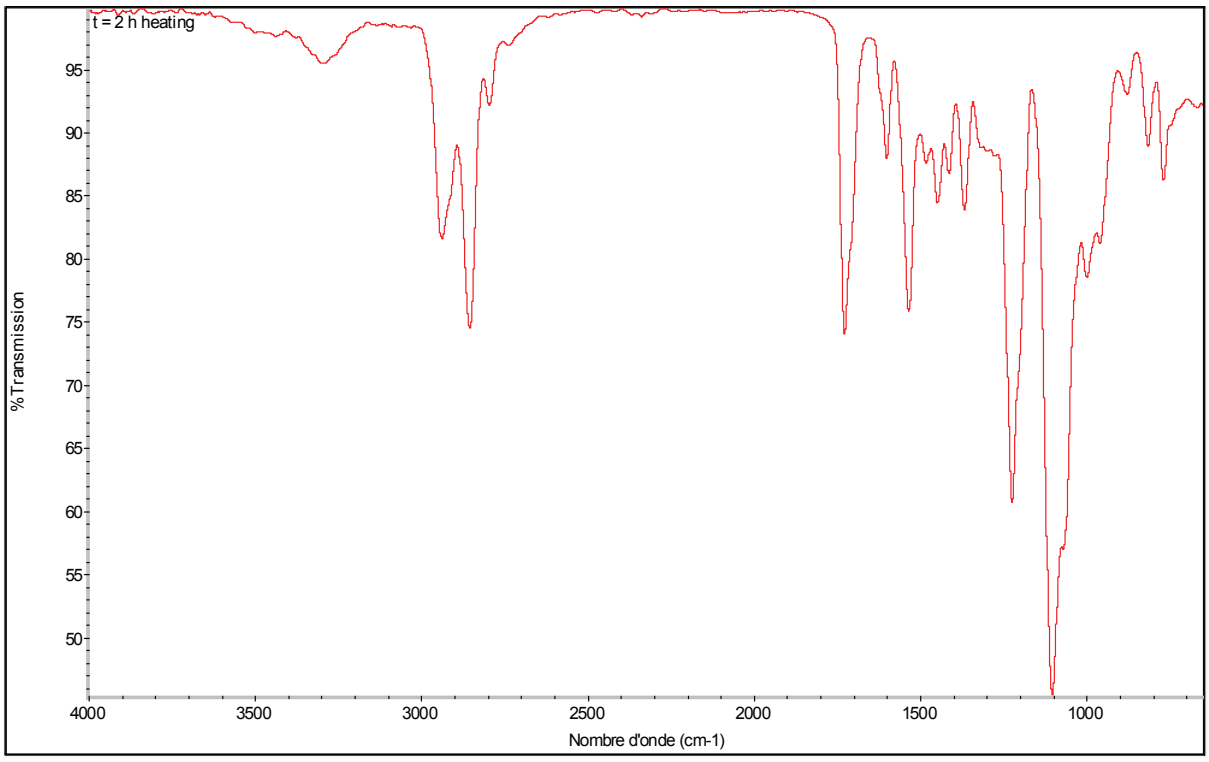


FT-IR spectrum of PU obtained without catalyst

➢ Synthesis of PU from **Ic** and **IIa** using MTBD-2BnNCO **2a** (1 mol%) as catalyst

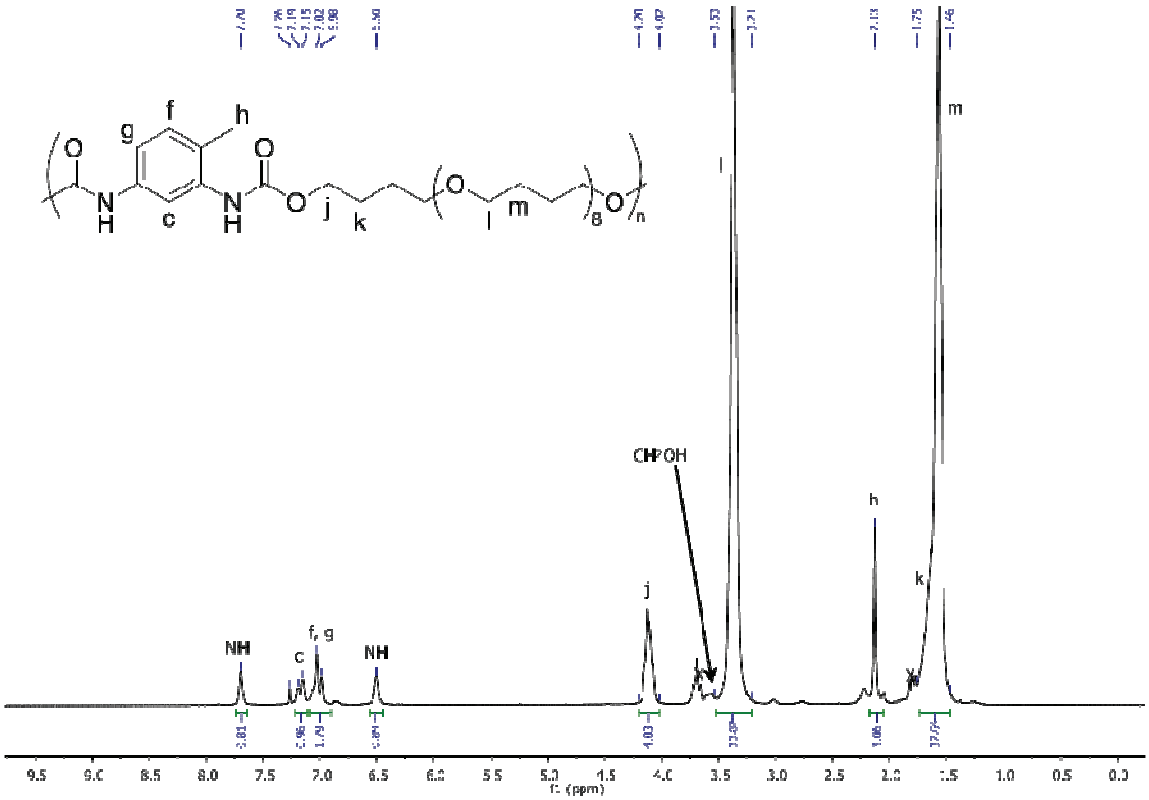


FT-IR spectra for the conversion monitoring (figure 2) using MTBD-2BnNCO (**2a**) as catalyst

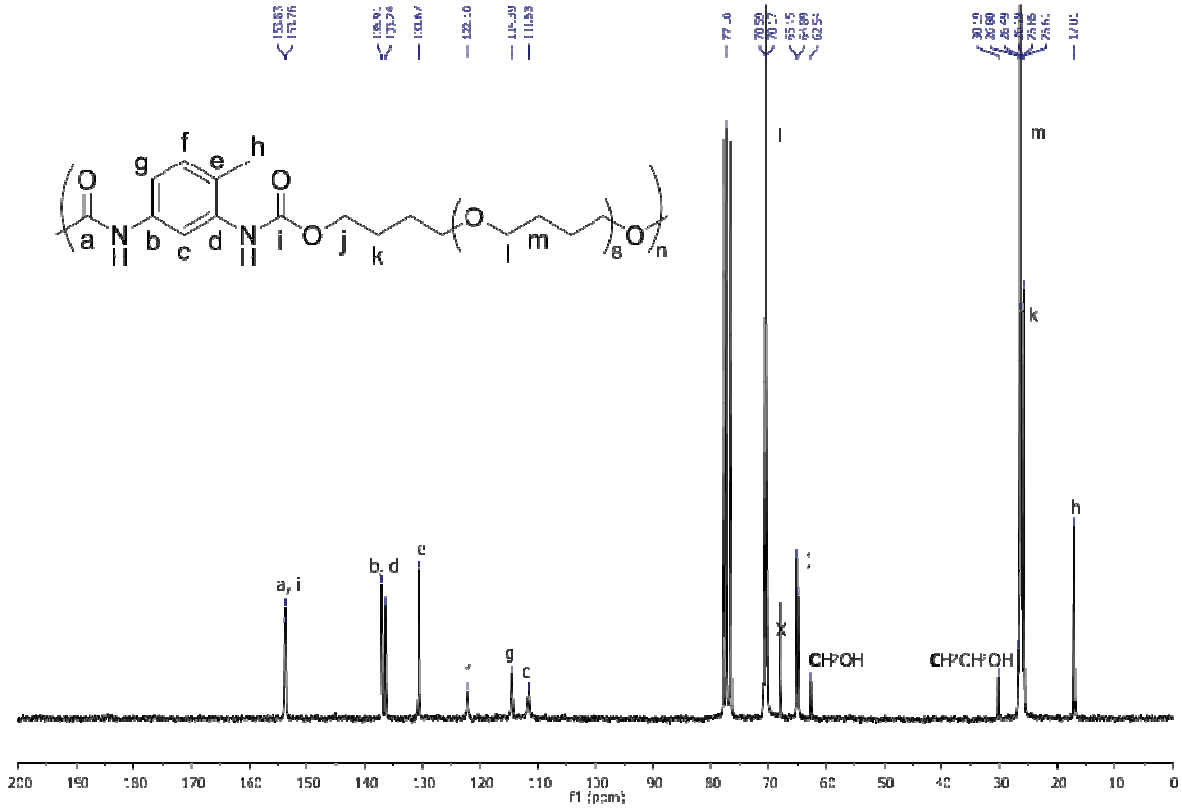


FT-IR spectrum of PU obtained using MTBD-2BnNCO (**2a**) as catalyst

- **Detailed RMN analysis of PU obtained from Ic and IIa**



^{1}H NMR spectrum ($CDCl_3$, 200 MHz, 298 K) PU obtained from **Ic** and **IIa** using **2a** as catalyst



^{13}C NMR spectrum ($CDCl_3$, 50 MHz, 298 K) of PU obtained from **Ic** and **IIa** using **2a** as catalyst