

Supporting Information For

***N*-Heterocyclic Carbene-Initiated Epoxide/Anhydride Ring-Opening Copolymerization: Effective and Selective Organoinitiators for the Production of Various Polyesters**

Gaël Printz,^[a] Redoy Gazi Shuvo,^[a] Antoine Schweizer,^[a] Dmytro Ryzhakov,^[b] Christophe Gourlaouen,^[c] Lielou Lantigner,^[b] Béatrice Jacques,^[a] Samir Messaoudi,^[b] Franck Le Bideau,^{*[b]}
Samuel Dagorne^{*[a]}

[a] Dr. G. Printz, A. Schweizer, Redoy Gazi Shuvo, Dr. B. Jacques, Dr. S. Dagorne

Institut de Chimie, CNRS – Université de Strasbourg

Strasbourg (France)

E-mail: dagorne@unistra.fr

[b] Dr. D. Ryzhakov, L. Lantigner, Dr. S. Messaoudi, Dr. F. Le Bideau

Université Paris-Saclay, CNRS, BioCIS

91400, Orsay (France)

E-mail: franck.lebideau@universite-paris-saclay.fr

[c] Dr. Christophe Gourlaouen

Laboratoire de Modélisation et Simulations Moléculaires, Université de Strasbourg, UMR 7140,

F-67000 Strasbourg, France

Table of Contents

General procedures and synthesis details	S3-S5
NMR spectra for species 1	S6-S7
Crystal data for species 1 (Table S1)	S8
ROCOP runs with SA (Table S2)	S9
GPC and NMR data for the produced polyesters	S10-S29
DSC data	S30
DFT computational details	S31-S34

General aspects. All experiments were performed under nitrogen atmosphere using standard Schlenk techniques or in a MBraun Unilab glove box. Toluene was first dried by using a solvent purification system (MBraun SPS) and stored for at least a couple of days over activated molecular sieves (4 Å) in a glovebox before use. All deuterated solvents (CD₂Cl₂, C₆D₆) were purchased from Eurisotope (CEA, Saclay, France), degassed under a N₂ flow, and stored over activated molecular sieves (4 Å) in a glovebox before use. All other chemicals were used as received. Epoxides CHO and PO were purchased on Sigma-Aldrich and were distilled twice prior to use under inert atmosphere. Anhydrides PA and SA were purchased on Sigma-Aldrich, recrystallized twice from CHCl₃/toluene, then sublimed twice under vacuum prior to storage under inert atmosphere. [PPN]Cl was purchased from Aldrich and used as is. Carbenes IPr, IMes and Cl-IPr were prepared according to literature procedures.^{1,2,3} NMR spectra were recorded by using BrukerAC 300, or 600 MHz NMR spectrometers in NMR tubes or in Teflon-valved J-Young NMR tubes at room temperature. Chemical shifts are given in ppm. Mass spectra were recorded at the Mass Spectrometry Department of the University of Strasbourg. Mass spectra were acquired by using a MALDI-TOF-TOF Autoflex II TOF-TOF (Bruker Daltonics, Bremen, Germany) equipped with a nitrogen laser ($\lambda = 337$ nm). An external multipoint calibration was performed before each measurement with a standard peptide mixture and a standard protein mixture (which depended on the mass range analyzed). Scan accumulation and data processing were performed with FlexAnalysis 3.4 software. *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DTCB) and 2,5-dihydroxybenzoic acid (DHB) was used as matrix for the analysis of the polyester samples. Size exclusion chromatography (SEC) analysis was performed by using a SEC system (with SEC columns temperature set at 30 °C) equipped with a Shimadzu RID10A refractometer detector using HPLC-grade THF as an eluent. For all GPC samples, 3 mg of the polymer sample is dissolved in 1 mL of THF and 25 μ L of the resulting solution is injected for analysis. Molecular weights and \bar{D} were calculated using polystyrene standards.

For the synthesis of monomers eugenyl glycidyl ether (EGE) and safrole oxide (SO),⁵ all reagents were obtained from commercial sources and used without further purification unless otherwise stated. Organic solutions were concentrated by rotary evaporation (house vacuum, *ca.* 40 Torr) at 30 °C, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed using glass plates pre-coated with silica gel 60 F254 (0.25 mm thickness) impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by UV light and/or by staining upon heating with KMnO₄ solution (1.6% potassium permanganate in conc. sulfuric acid), vaniline solution (15 g of vanillin, 250 mL of EtOH, 2.5 mL conc. H₂SO₄) and bromocresol green solution (0.1 g bromocresol green in 500 mL ethanol and 5 mL 0.1 M NaOH). Flash column chromatography was performed as described by Still et al.,⁴ employing silica gel (60 Å pore size, 40-63 mm). IR spectra were recorded as thin films for oils and for solids by the reflexion method on a IRAffinity-1S FTIR spectrometer. The ¹H, ¹³C {¹H} and ¹⁹F NMR spectra were recorded in CDCl₃ on Bruker Avance 300 and 400 spectrometers. Chemical shifts

¹ L. Jafarpour, E. D. Stevens, S. P. Nolan, *J. Organomet. Chem.* **2000**, 606, 49.

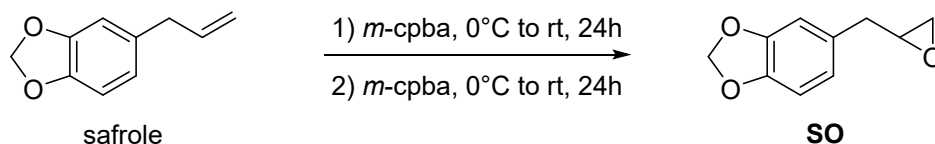
² A. J. Arduengo III, H.V.R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, 114, 5530.

³ A. J. Arduengo, R. Krafczyk, R. Schmutzler, *Tetrahedron* **1999**, 55, 14523.

⁴ W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, 43, 2923.

are reported in ppm relative to the solvent residual peak in CDCl_3 (δ 7.26) for ^1H NMR. For the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, the solvent signals of CDCl_3 (δ 77.16) were used as the internal standard. A combination of COSY, HSQC, HMBC and nOe experiments was used to aid assignment when necessary. High resolution mass spectra (HRMS) were performed on an Agilent 1260 Infinity system with a quadrupole time-of-flight (Q-TOF) mass analyser. Mass spectra were realized by electrospray impact (ESI) and atmospheric pressure chemical ionisation (APCI).

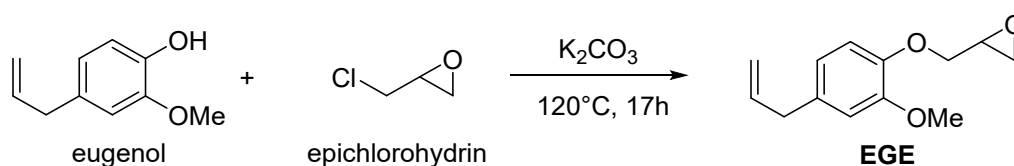
Synthesis of racemic 5-(oxiran-2-ylmethyl)benzo[d][1,3]dioxole (safrole oxide, SO).



m-Chloroperbenzoic acid (50% = 16.78 g, 48.6 mmol) was slowly added to a solution of safrole (60.6 g, 40.5 mmol) in chloroform (300 mL) at 0 °C. The reaction mixture was stirred at room temperature for 24 hours, cooled to 0°C and *m*-chloroperbenzoic acid (50% =, 16.78 g, 48.6 mmol) was slowly added. The reaction mixture was stirred at room temperature for another 24 h and evaporated to dryness. The resulting oil was purified by flash chromatography two times (PE/EtOAc = 90:10 and PE/DCM = 70:30 for the second purification) to give SO as a yellow liquid (3.5 g, 48 %). The ^1H NMR spectrum shows the presence of water (6%, 1.56 ppm). The NMR data are consistent with the literature.⁵

^1H NMR (300 MHz, CDCl_3): δ 6.81–6.63 (m, 3 H), 5.93 (s, 2 H), 3.15–3.07 (m, 1 H), 2.87–2.70 (m, 3 H), 2.53 (dd, J = 4.5, 2.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 147.7, 146.3, 130.8, 121.8, 109.4, 108.2, 100.8, 52.4, 46.6, 38.3 ppm.

Synthesis of racemic 2-((4-allyl-2-methoxyphenoxy)methyl)oxirane (eugenyl glycidyl ether, EGE).



A mixture of eugenol (17.2 g, 105 mmol) and K_2CO_3 (17.4 g, 125 mmol) in epichlorohydrin (44 ml, 530 mmol) was stirred at 120 °C for 17 hours. Excess epichlorohydrin was carefully evaporated to dryness. The resulting mixture was purified by flash chromatography (PE/EtOAc = 70:30) to afford EGE (13.1 g, 57%) as a white solid.

General procedure for epoxide/anhydride ROCOP by NHCs. All polymerization experiments were prepared under a nitrogen atmosphere in a glove box. The appropriate amount of epoxide/anhydride monomers and the NHC initiator (10 μmol) were charged in a vial

⁵ L.-C. Shen, S.-Y. Chiang, Ho, I.-T.; Wu, K.-Y.; Chung, W.-S. *Eur J Org Chem* **2012**, 2012, 792.

equipped with a Teflon screw-cap. A magnetic stirring bar was added to the reaction mixture, and the latter was then immersed in preheated oil bath at 90 °C. It was stirred for the appropriate time with monomer conversion being periodically monitored by ¹H NMR spectroscopy. After the reaction, the crude residue was dissolved at room temperature in a minimum of CH₂Cl₂, and an excess of methanol was added to quench the reaction mixture leading to polymer precipitation. The polymer was washed three times with methanol, dried under vacuum and analysed by using ¹H NMR spectroscopy, GPC analysis and MALDI-TOF mass spectrometry.

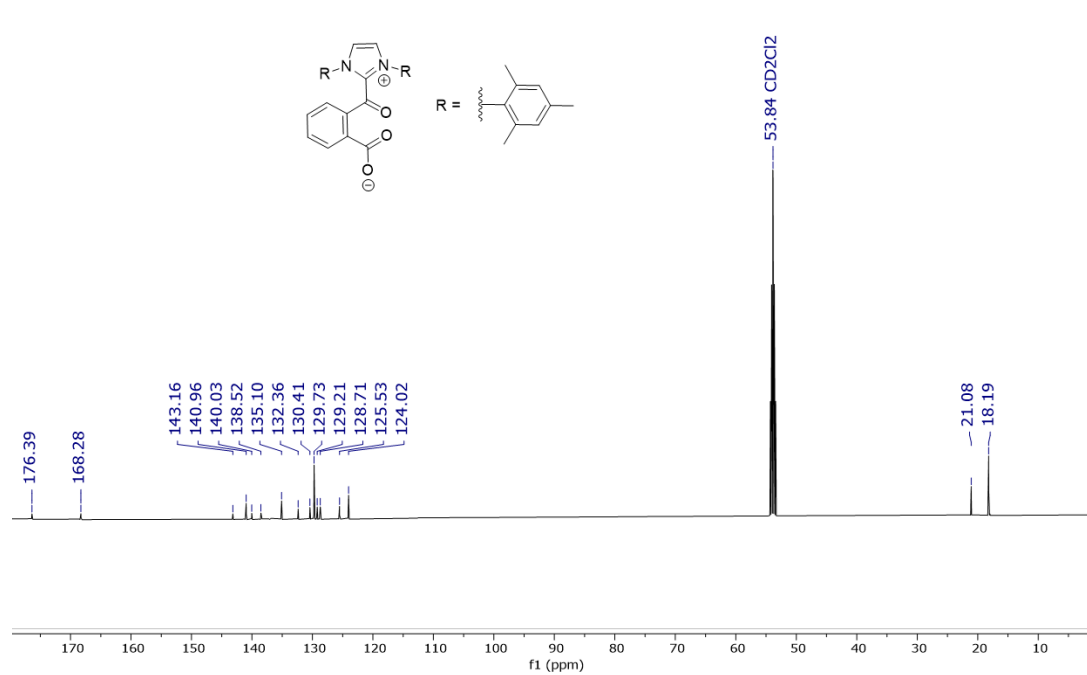
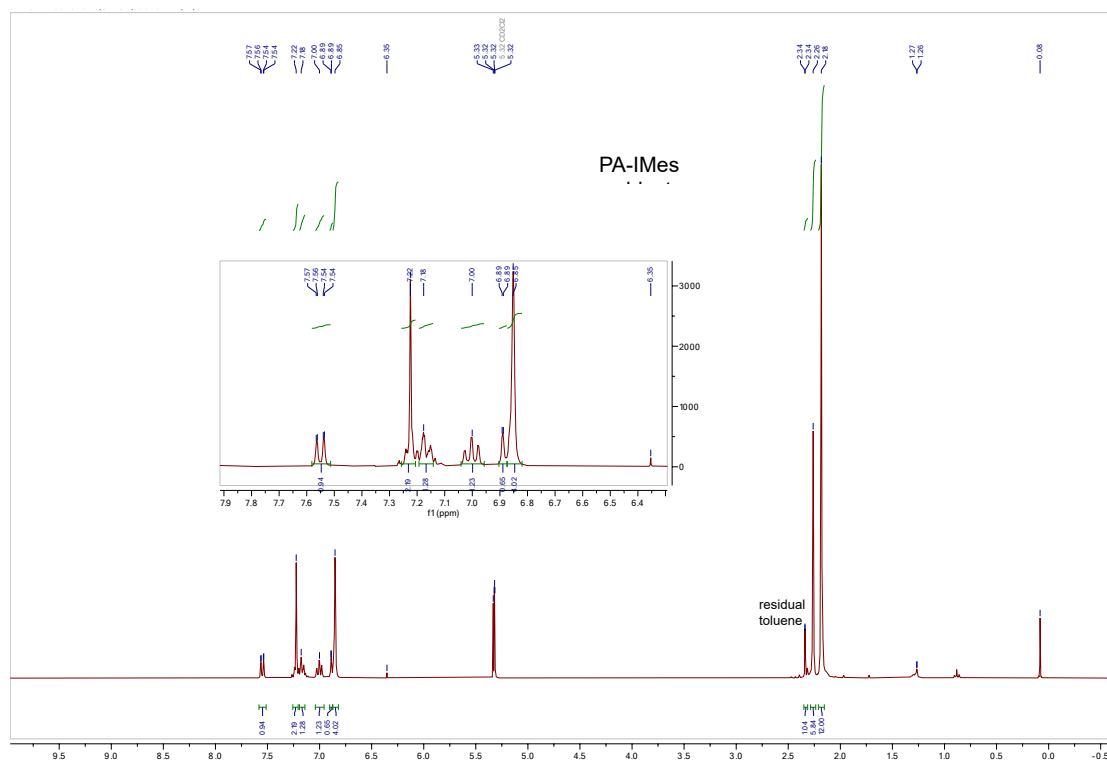
Synthesis of PA-IMes (1). In the N₂-filled glovebox were prepared a vial containing a solution of PA (29.4 mg, 2.0 mmol) in 1 mL toluene, and a vial containing IMes (60 mg, 2.0 mmol) in 1 mL toluene. Using a Pasteur pipette, the PA solution was added to the carbene solution upon stirring at room temperature. A precipitate formed instantly upon addition and the mixture was left an additional 30 min under stirring. Toluene was removed using a Pasteur pipette and the precipitate was washed twice with toluene (2x2 mL). Drying the resulting precipitate under vacuum overnight led to pure PA-IMes (**1**, 79% yield) as deduced from all characterization data. XRD-suitable single crystals of **1** were grown from a 2/1 CH₂Cl₂/pentane solution stored at -30 °C. Pure **1** was analyzed by ¹H, ¹³C, HMBC and HSQC NMR in CD₂Cl₂, all consistent with the proposed structure. Elemental analysis for **1** (C₂₉H₂₈N₂O₃): calcd. C, 76.97; H, 6.24; N, 6.19. Found. C, 77.04; H, 6.01; N, 6.32. ¹H RMN (CD₂Cl₂, 400 MHz) δ: 2.18 (s, 12H), 2.26 (s, 6H), 6.85 (s, 4H), 6.88 (d, 1H), 7.00 (t, J = 6,6 Hz, 1H), 7.17 (t, 1H), 7.23 (s, 2H), 7,55 (d, J = 6,6 Hz, 1H). ¹³C{¹H} RMN, (CD₂Cl₂, 100 MHz) δ: 18.2, 21.1, 124.0, 125.5, 128.7, 129.2, 129.7, 130.4, 132.4, 135.1, 138.5, 140.0, 141.0, 143.2, 168.3, 176.4.

X-ray crystallography analysis of species 1. A crystal of **1** was placed in oil, and a single crystal was selected, mounted on a micromount and placed in a low-temperature N₂ stream. X-Ray diffraction data collection was carried out on a Bruker PHOTON-III DUO CPAD diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 38 mm. The cell parameters were determined (APEX4 software)⁶ from reflections taken from one set of 180 frames, each at 1s exposure. The structures were solved using the program SHELXT-2014.⁷ The refinement and all further calculations were carried out using SHELXL-2014.⁸ The hydrogen atoms of the dichloromethane solvent were located from Fourier difference, but they were not refined. The other H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on *F*². A semi-empirical absorption correction was applied using SADABS in APEX4; transmission factors: T_{min}/T_{max} = 0.7161/0.7460.

⁶ “M86-EXX278V1 APEX4 User Manual”, Bruker Corporation, 2021.

⁷ G. M. Sheldrick, *Acta Cryst.* **2015**, A71, 3-8.

⁸ G. M. Sheldrick, *Acta Cryst.* **2015**, C71, 3-8.



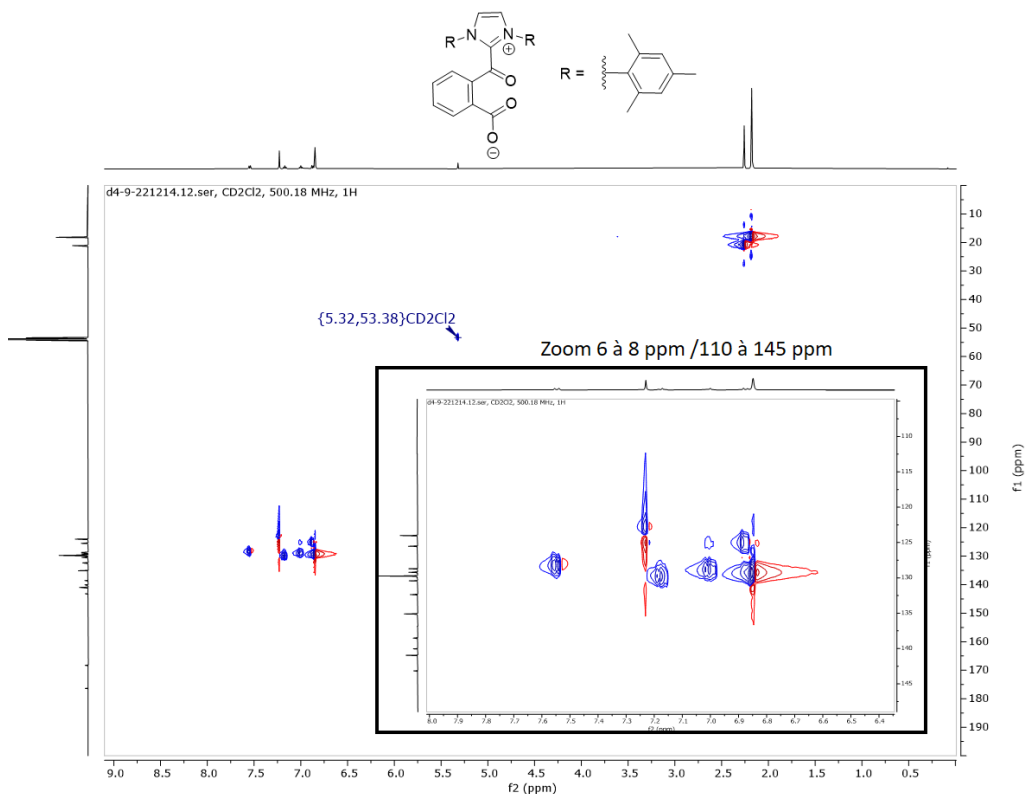


Figure S3. 2D HSQC NMR spectrum (CD₂Cl₂, 500 MHz) of isolated PA-IMes produced by reaction of 1 equiv of IMes with PA.

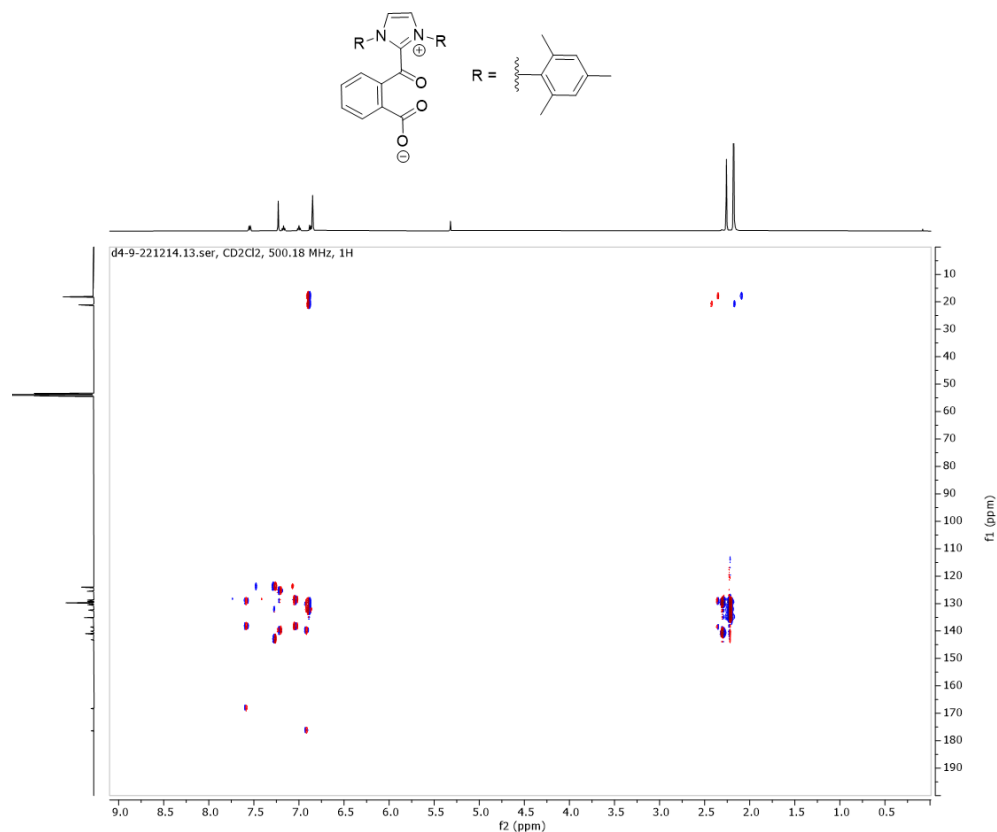


Figure S4. 2D HSQC NMR spectrum (CD₂Cl₂, 500 MHz) of isolated PA-IMes produced by reaction of 1 equiv of IMes with PA.

Table S1. Crystal data and structure refinement for IMes-PA (1) (CCDC 2367268).

Empirical formula	C ₅₉ H ₅₈ Cl ₂ N ₄ O ₆
Formula weight	989.99
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 8.0672(3) Å alpha = 90 deg. b = 13.0590(7) Å beta = 90.676(2) deg. c = 24.6529(12) Å gamma = 90 deg.
Volume	2597.0(2) Å ³
Z, Calculated density	2, 1.266 Mg/m ³
Absorption coefficient	0.181 mm ⁻¹
F(000)	1044
Crystal size	0.200 x 0.100 x 0.080 mm
Theta range for data collection	2.272 to 30.036 deg.
Limiting indices	-11 ≤ h ≤ 11, -18 ≤ k ≤ 18, -34 ≤ l ≤ 34
Reflections collected / unique	104745 / 7609 [R(int) = 0.0697]
Completeness to theta	25.242 100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7460 and 0.7161
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7609 / 0 / 331
Goodness-of-fit on F ²	1.025
Final R indices [I > 2sigma(I)]	R1 = 0.0514, wR2 = 0.1210
R indices (all data)	R1 = 0.0732, wR2 = 0.1359
Extinction coefficient	n/a
Largest diff. peak and hole	0.431 and -0.867 e.Å ⁻³

Table S2. ROCOP of SA and CHO/PO initiated by NHCs IMes, IPr and Cl-IPr ^a

	NHC initiator	Epoxide	SA/Epoxide/ NHC ratio	Time (h)	Conv. SA (%) ^b	Ester linkage (%) ^b	<i>M</i> _n (kg/mol) ^c	<i>D</i> ^c
1	IPr	CHO	60:70:1	16	94	88	5.75	1.52
2	IMes	CHO	250:300:1	16	96	86	2.61	1.79
3	IPrCl	CHO	250:300:1	16	87	82	2.81	1.53
4	IPr	CHO	250:300:1	16	92	81	2.33	1.37
5	IPr ^d	CHO	250:300:1	16	33	80	1.45	1.24
6	IPr	PO	250:300:1	16	96	> 98	5.92	1.82

^a Conditions (unless indicated otherwise): neat conditions (no solvent), 90 °C. ^b determined by ¹H NMR.

^c Determined by GPC analysis (THF, room temperature) using polystyrene standards. ^d ROCOP performed at 70 °C.

Data for the produced polyesters

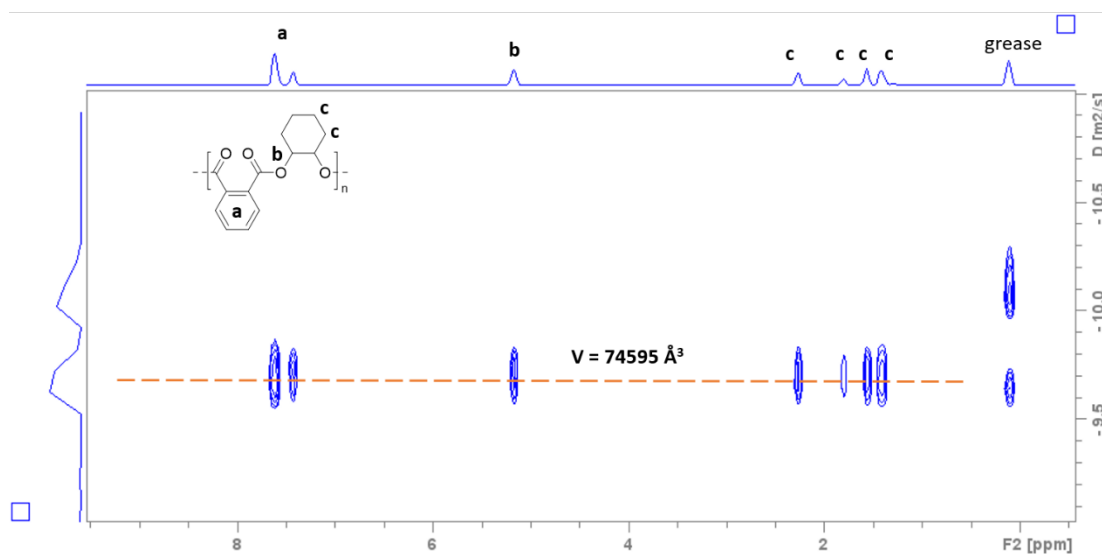


Figure S5. ^1H DOSY NMR (CDCl_3 , 600 MHz) of isolated poly(PA-*alt*-CHO) formed from the ROCOP of PA and CHO initiated by IPr (PA/CHO/IPr (60/70/1), 90 °C, 16 h, 95% conversion of PA, $M_n = 10.2 \text{ kg mol}^{-1}$, $D = 1.05$). The estimated volume ($V = 74595 \text{ \AA}^3$) was deduced from the measured diffusion coefficient ($D = 1.55 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$).

Figure S6. ^1H NMR spectrum (300 MHz, CDCl_3) of isolated poly(PA-*alt*-CHO) formed from the ROCOP of PA and CHO initiated by IPr. Conditions: 60/70/1 (PA/CHO/IPr), no solvent, 90 °C, 16 h (95 % conversion of PA).

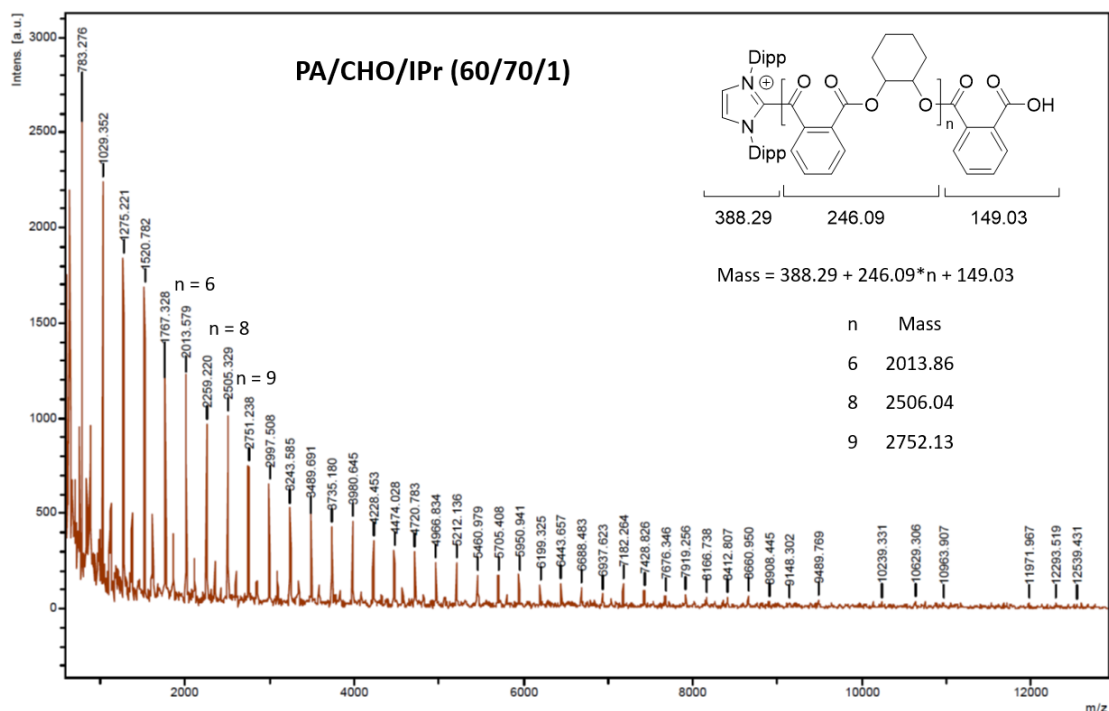


Figure S7. MALDI-TOF mass spectrum data for isolated p(PA-CHO) formed from the ROCOP of PA and CHO initiated by IPr. Conditions: 60/70/1 (PA/CHO/IPr), no solvent, 90 °C, 16 h (95 % conversion of PA).

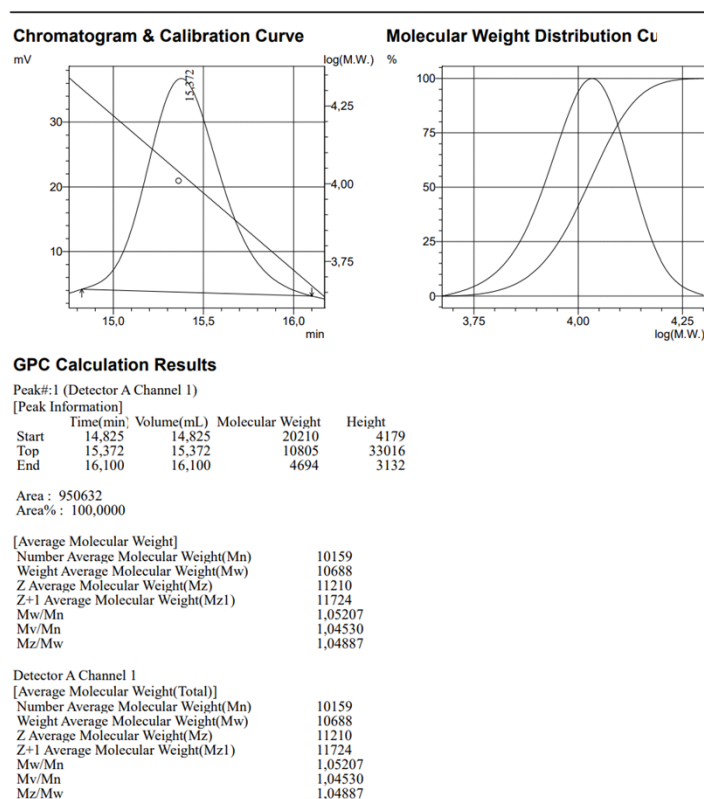


Figure S8. GPC traces of isolated p(PA-CHO) formed from the ROCOP of PA and CHO initiated by IPr. Conditions: 60/70/1 (PA/CHO/IPr), no solvent, 90 °C, 16 h (95 % conversion of PA).

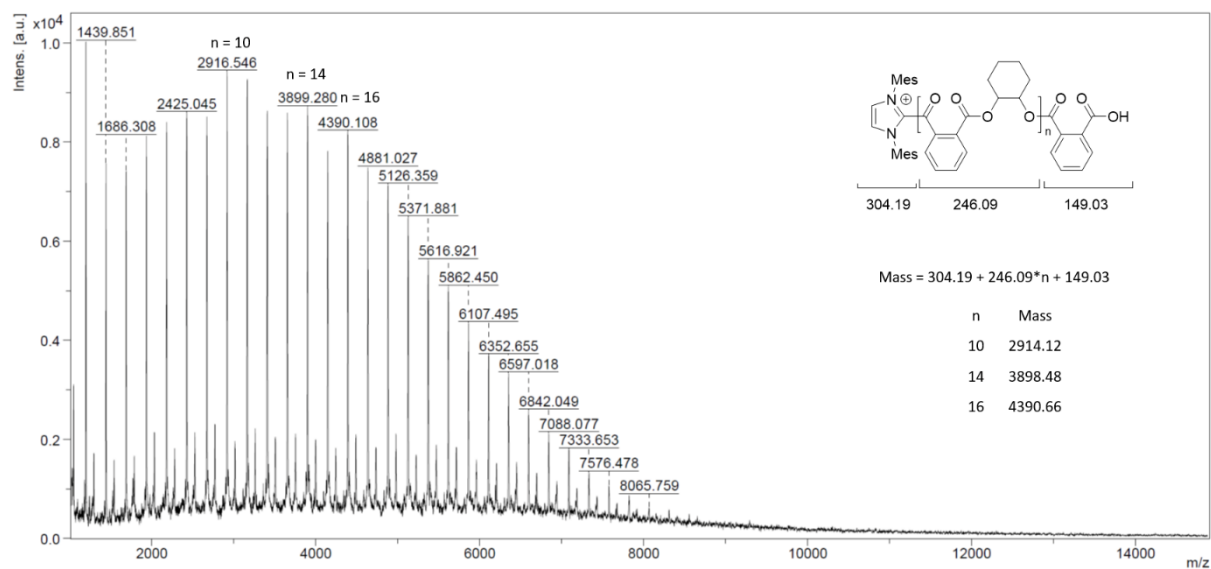


Figure S9. MALDI-TOF mass spectrum data for isolated p(PA-CHO) formed from the ROCOP of PA and CHO initiated by IMes. Conditions: 60/70/1 (PA/CHO/IPr), no solvent, 90 °C, 16 h (95 % conversion of PA).

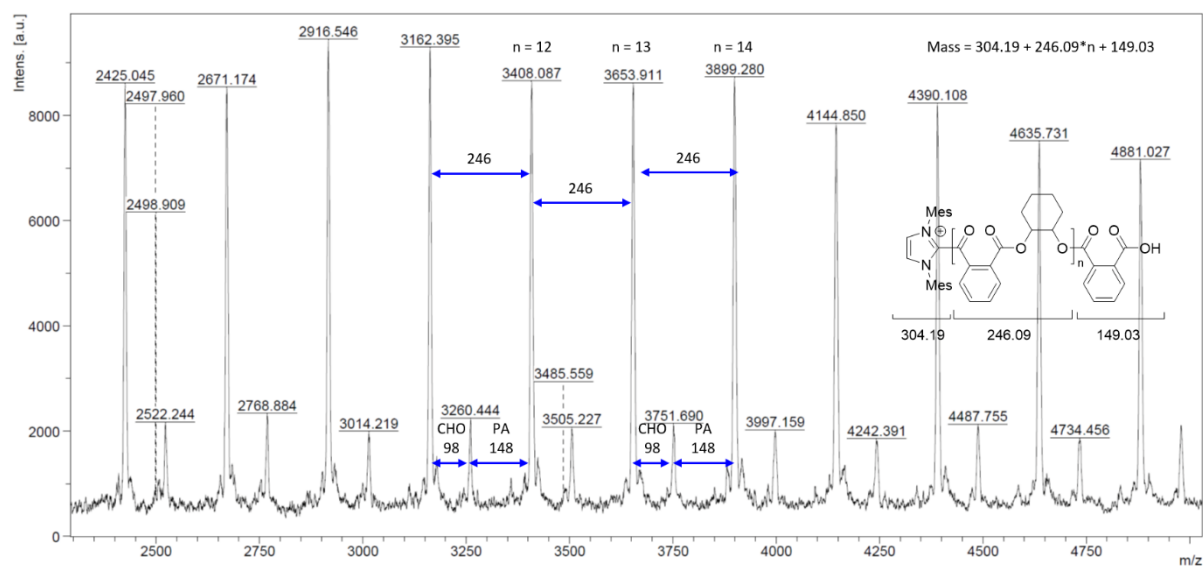


Figure S10. Zoom-in of the MALDI-TOF mass spectrum data for isolated poly(PA-*alt*-CHO) formed from the ROCOP of PA and CHO initiated by IMes. Conditions: 60/70/1 (PA/CHO/IPr), no solvent, 90 °C, 16 h (95 % conversion of PA).

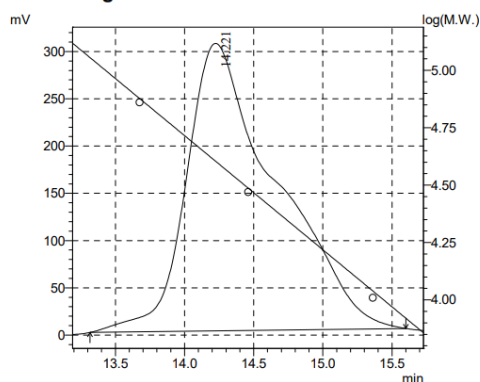
Figure S11. ^1H NMR spectrum (300 MHz, CDCl_3) of isolated poly(PA-*alt*-CHO) formed from the ROCOP of PA and CHO initiated by IPr. Conditions: 250/300/1 (PA/CHO/IPr), no solvent, 90 °C, 16 h (100 % conversion of PA).

Figure S12. ^1H NMR spectrum (300 MHz, CDCl_3) of isolated poly(PA-*alt*-CHO) formed from the ROCOP of PA and CHO initiated by IPrCl. Conditions: 250/300/1 (PA/CHO/IPr), no solvent, 90 °C, 16 h (100 % conversion of PA).

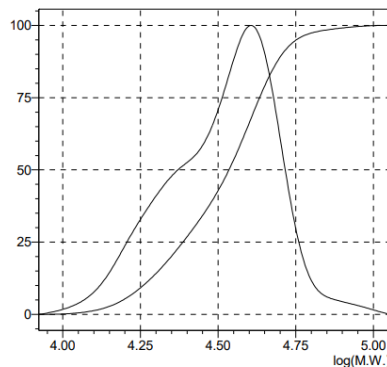
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 Method Filename : gpc.lcm
 Batch Filename :
 Report Filename : Report_template.lcr
 Date Acquired : 02/04/2024 16:50:26
 Data Processed : 02/04/2024 17:15:29

Chromatogram & Calibration Curve



Molecular Weight Distribution Curve



GPC Calculation Results

Peak#:1 (Detector A Ch1)

[Peak Information]

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End	15.600	15.600	8322	7003

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Area% : 100.0000

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Weight Average Molecular Weight(Mw)	34932
Z Average Molecular Weight(Mz)	40212
Z+1 Average Molecular Weight(Mz1)	45621
Mw/Mn	1.17609
Mv/Mn	1.15219
Mz/Mw	1.15115

Detector A Ch1

[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	29702
Weight Average Molecular Weight(Mw)	34932
Z Average Molecular Weight(Mz)	40212
Z+1 Average Molecular Weight(Mz1)	45621
Mw/Mn	1.17609
Mv/Mn	1.15219
Mz/Mw	1.15115

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Figure S13. GPC traces of isolated p(PA-CHO) formed from the ROCOP of PA and CHO initiated by PA-IMes. Conditions: 250/300/1 (PA/CHO/IPr), no solvent, 90 °C, 16 h (97 % conversion of PA).

Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR of isolated poly(PA-*alt*-CHO) formed from the ROCOP of PA and CHO initiated by PA-IMes. Conditions: 250/300/1 (PA/CHO/IPr), no solvent, 90 °C, 16 h (97 % conversion of PA).

Figure S15. DEPT ^{13}C NMR (125 MHz, CDCl_3) of isolated p(PA-CHO) formed from the ROCOP of PA and CHO initiated by PA-IMes. Conditions: 250/300/1 (PA/CHO/IPr), no solvent, 90 °C, 16 h (97 % conversion of PA).

Figure S16. ^1H NMR spectrum (300 MHz, CDCl_3) of isolated poly(PA-*alt*-PO) formed from the ROCOP of PA and PO initiated by IPr. Conditions: 250/300/1 (PA/PO/IPr), no solvent, 90 °C, 16 h (80 % conversion of PA).

Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz, CDCl_3) of isolated poly(PA-*alt*-PO) formed from the ROCOP of PA and PO initiated by IPr. Conditions: 250/300/1 (PA/PO/IPr), no solvent, 90 °C, 16 h (80 % conversion of PA).

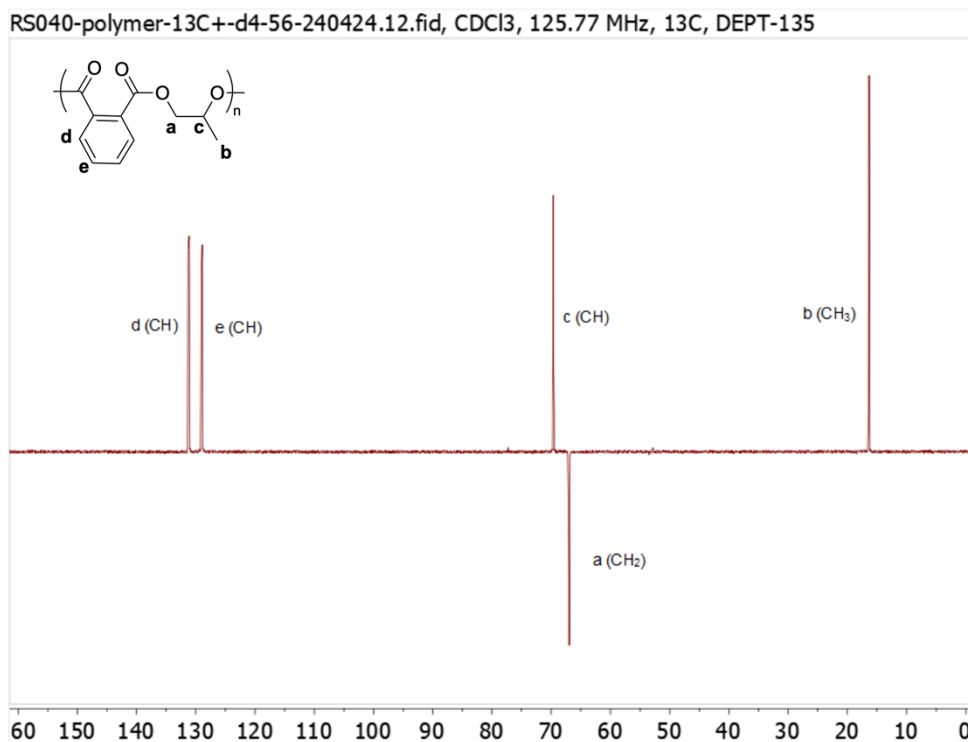


Figure S18. DEPT ¹³C NMR spectrum (125 MHz, CDCl₃) of isolated p(PA-*alt*-PO) formed from the ROCOP of PA and PO initiated by IPr. Conditions: 250/300/1 (PA/PO/IPr), no solvent, 90 °C, 16 h (80 % conversion of PA).

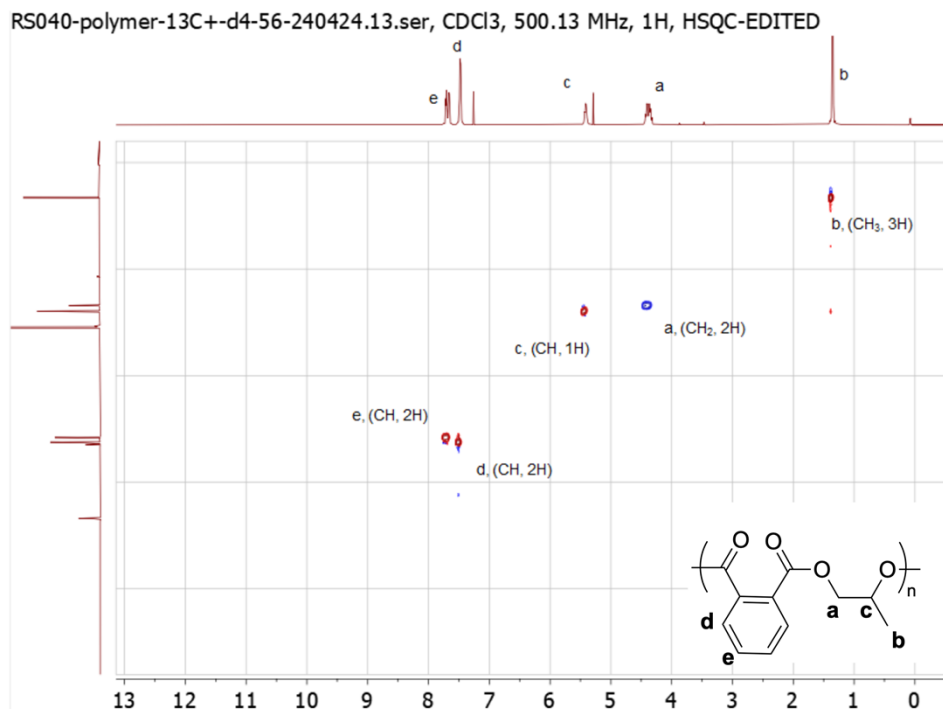


Figure S19. HSQC NMR spectrum (500 MHz, CDCl₃) of isolated p(PA-*alt*-PO) formed from the ROCOP of PA and PO initiated by IPr. Conditions: 250/300/1 (PA/PO/IPr), no solvent, 90 °C, 16 h (80 % conversion of PA).

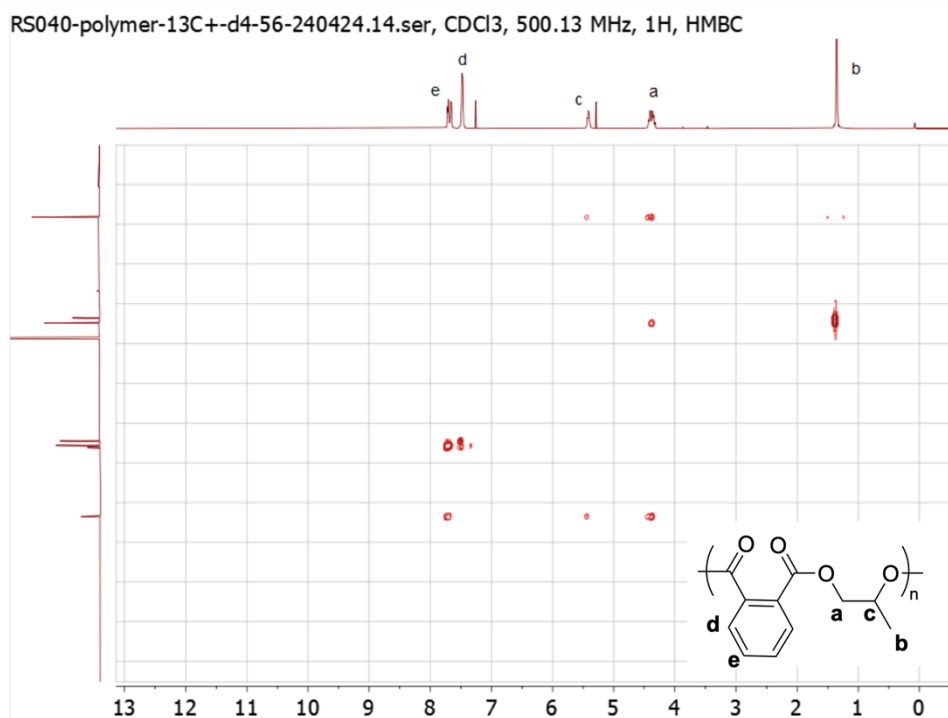


Figure S20. HMBC NMR spectrum (500 MHz, CDCl₃) of isolated p(PA-*alt*-PO) formed from the ROCOP of PA and PO initiated by IPr. Conditions: 250/300/1 (PA/PO/IPr), no solvent, 90 °C, 16 h (80 % conversion of PA).

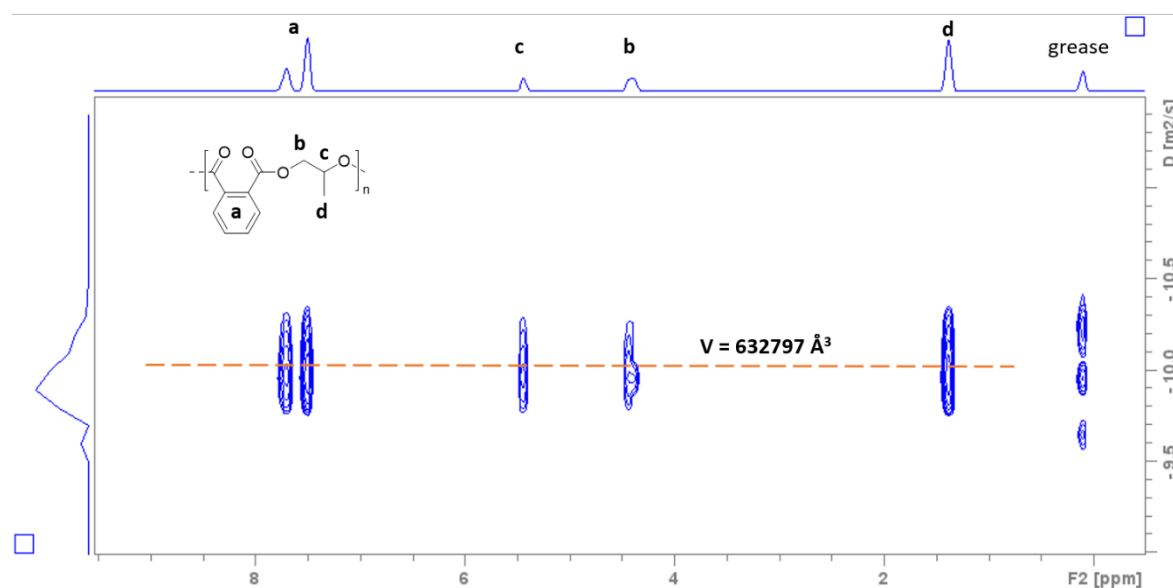
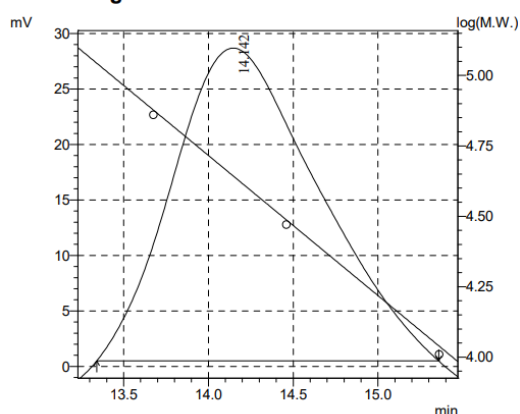


Figure S21. ¹H DOSY NMR (CDCl₃, 600 MHz) of isolated poly(PA-*alt*-PO) formed from the ROCOP of PA and PO initiated by IMes (PA/PO/IMes (250/300/1), 90 °C, 16 h, 83% conversion of PA, M_n GPC = 33.05 kg mol⁻¹, \bar{D} = 1.21). The estimated volume ($V = 632797 \text{ \AA}^3$) was deduced from the measured diffusion coefficient ($D = 7.60 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$).

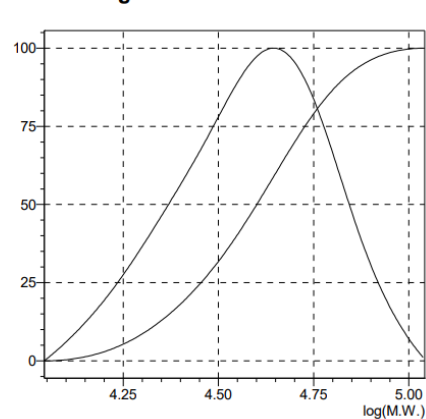
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Chromatogram & Calibration Curve



Molecular Weight Distribution Curve



GPC Calculation Results

Peak#:1 (Detector A Ch1)

[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
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Top	14.142	14.142	44167	28185
End	15.358	15.358	10974	492

Area : 1674633

Area% : 100.0000

[Average Molecular Weight]

Number Average Molecular Weight(Mn)	34993
Weight Average Molecular Weight(Mw)	42484
Z Average Molecular Weight(Mz)	50157
Z+1 Average Molecular Weight(Mz1)	57382
Mw/Mn	1.21405
Mv/Mn	1.18444
Mz/Mw	1.18062

Detector A Ch1

[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	34993
Weight Average Molecular Weight(Mw)	42484
Z Average Molecular Weight(Mz)	50157
Z+1 Average Molecular Weight(Mz1)	57382
Mw/Mn	1.21405
Mv/Mn	1.18444
Mz/Mw	1.18062

C:\LabSolutions\Data\Shuvo\Results\rs040crude.lcd

Figure S22. GPC trace of isolated p(PA-*alt*-PO) formed from the ROCOP of PA and PO initiated by IPr. Conditions: 250/300/1 (PA/CHO/IPr), no solvent, 90 °C, 16 h (80 % conversion of PA).

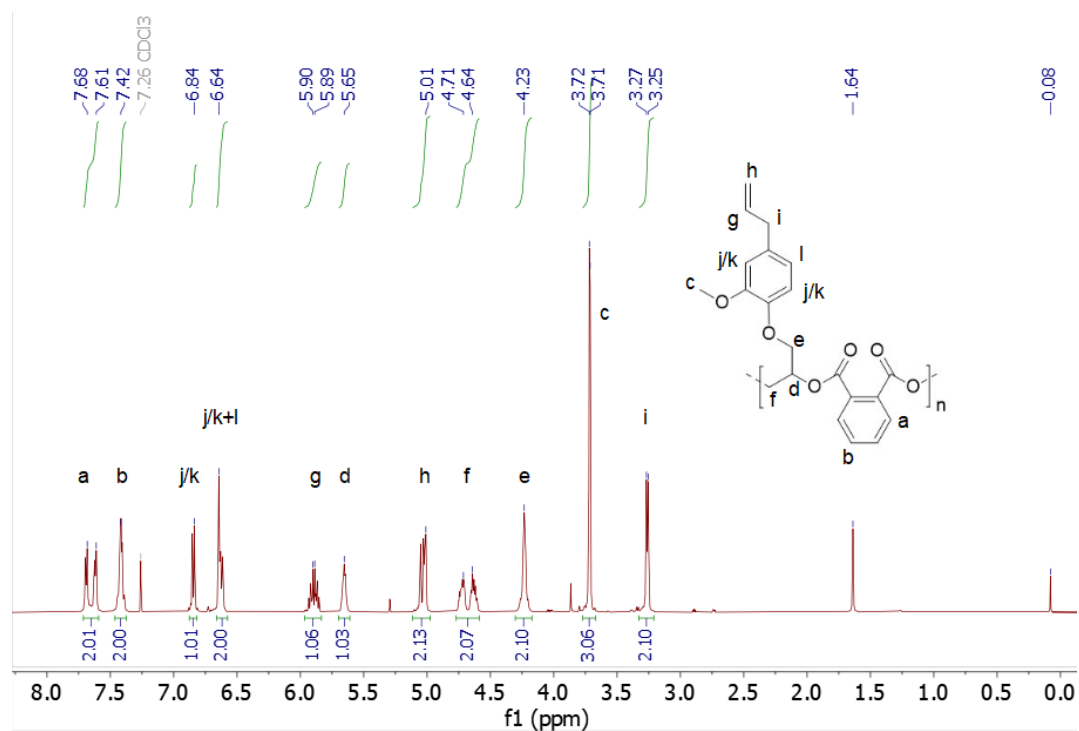
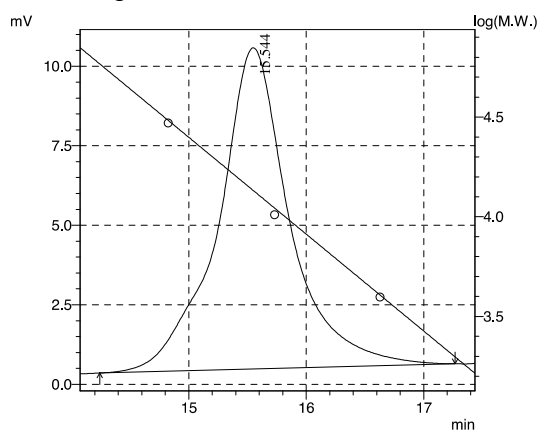


Figure S23. ¹H NMR spectrum (500 MHz, CDCl₃) of isolated p(PA-*alt*-EGE) formed from the ROCOP of PA and EGE initiated by IPr. Conditions: 250/300/1 (PA/CHO/IPr), no solvent, 90 °C, 16 h (100 % conversion of PA).

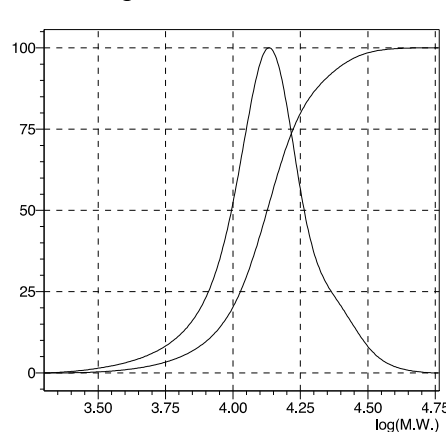
==== Shimadzu LCsolution GPC Analysis Report ====

Acquired by : Admin
 Sample Name : GP621A BRUT
 Sample ID : GP621A BRUT
 Vial# :
 Injection Volume : 100 uL
 Data Filename : GP621A BRUT.lcd
 Method Filename : gpc.lcm
 Batch Filename :
 Report Filename : Report_template.lcr
 Date Acquired : 08/09/2022 17:13:59
 Data Processed : 08/09/2022 17:37:37

Chromatogram & Calibration Curve



Molecular Weight Distribution Curve



GPC Calculation Results

Peak#:1 (Detector A Ch1)

[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	14.242	14.242	58430	356
Top	15.544	15.544	13612	10102
End	17.267	17.267	1982	644

Area : 428543
Area% : 100.0000

[Average Molecular Weight]

Number Average Molecular Weight(Mn)	12113
Weight Average Molecular Weight(Mw)	14370
Z Average Molecular Weight(Mz)	16781
Z+1 Average Molecular Weight(Mz1)	19592
Mw/Mn	1.18630
Mv/Mn	1.16088
Mz/Mw	1.16778

Detector A Ch1

[Average Molecular Weight(Total)]

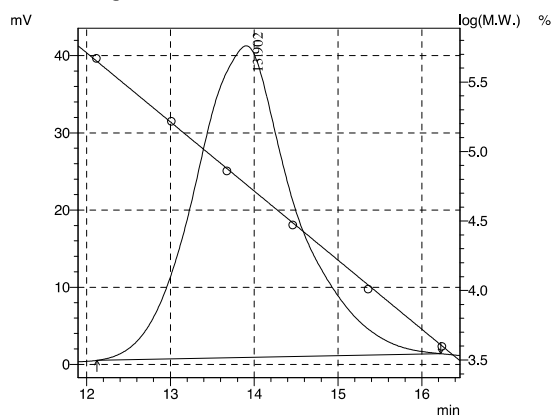
Number Average Molecular Weight(Mn)	12113
Weight Average Molecular Weight(Mw)	14370
Z Average Molecular Weight(Mz)	16781
Z+1 Average Molecular Weight(Mz1)	19592
Mw/Mn	1.18630
Mv/Mn	1.16088
Mz/Mw	1.16778

Figure S24. GPC traces of crude p(PA-*alt*-EGE) produced from the ROCOP of PA and EGE initiated by IPr. Conditions: 70/85/1 (PA/EGE/IPr), no solvent, 90 °C, 5 h (83 % conversion of PA).

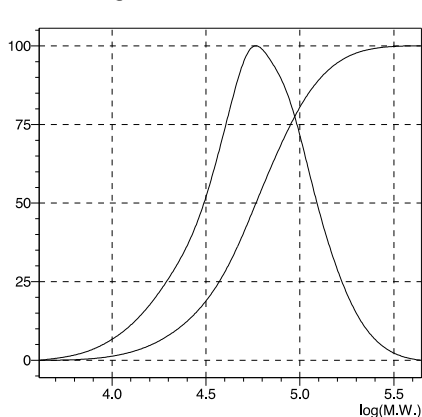
==== Shimadzu LCsolution GPC Analysis Report ====

Acquired by : Admin
 Sample Name : rs068polymer
 Sample ID : rs068polymer
 Vail# :
 Injection Volume : 100 uL
 Data Filename : rs068polymer.lcd
 Method Filename : gpc.lcm
 Batch Filename :
 Report Filename : Report_template.lcr
 Date Acquired : 04/06/2024 17:31:49
 Data Processed : 04/06/2024 17:56:52

Chromatogram & Calibration Curve



Molecular Weight Distribution Curve



GPC Calculation Results

Peak#:1 (Detector A Ch1)

[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	12.125	12.125	444776	527
Top	13.902	13.902	58180	40368
End	16.225	16.225	4068	1389

Area : 3338290
 Area% : 100.0000

[Average Molecular Weight]

Number Average Molecular Weight(Mn)	43532
Weight Average Molecular Weight(Mw)	69965
Z Average Molecular Weight(Mz)	102548
Z+1 Average Molecular Weight(Mz1)	141100
Mw/Mn	1.60721
Mv/Mn	1.51836
Mz/Mw	1.46571

Detector A Ch1

[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	43532
Weight Average Molecular Weight(Mw)	69965
Z Average Molecular Weight(Mz)	102548
Z+1 Average Molecular Weight(Mz1)	141100
Mw/Mn	1.60721
Mv/Mn	1.51836
Mz/Mw	1.46571

Figure S25. GPC traces of crude p(PA-*alt*-EGE) produced from the ROCOP of PA and EGE initiated by IPr. Conditions: 250/300/1 (PA/EGE/IPr), no solvent, 90 °C, 16 h (100 % conversion of PA).

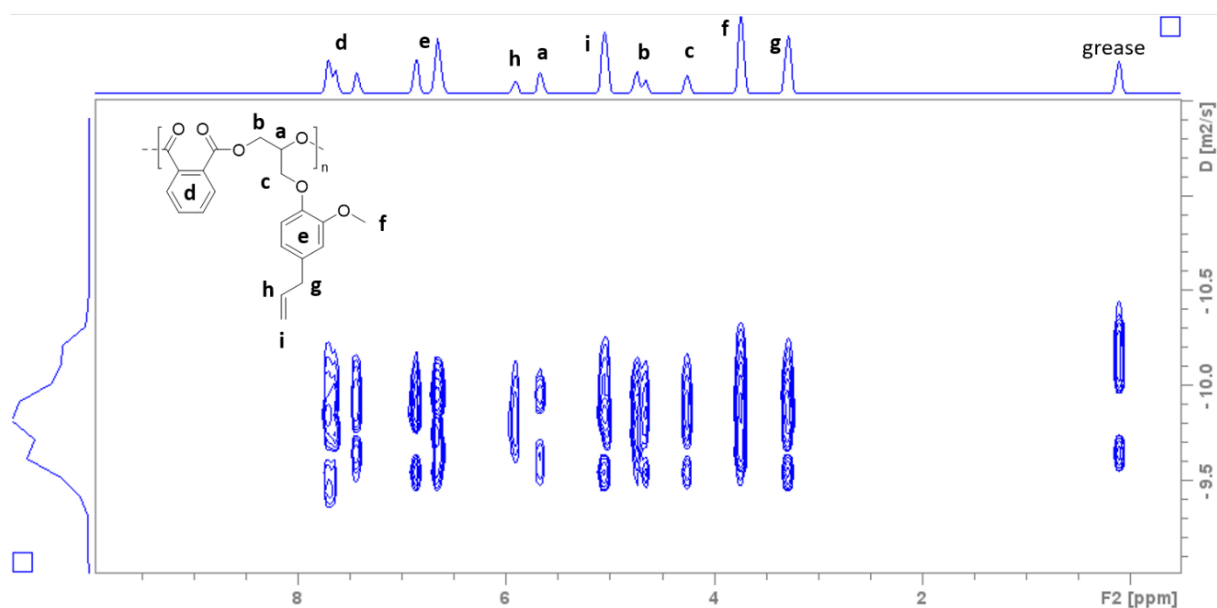


Figure S26. ^1H DOSY NMR (CDCl_3 , 600 MHz) of isolated poly(PA-*alt*-EGE) formed from the ROCOP of PA and EGE initiated by IPr (PA/EGE/IPr (70/85/1), 90 °C, 5 h, 100% conversion of PA, $M_{n, \text{GPC}} = 43.5 \text{ kg mol}^{-1}$, $\bar{D} = 1.6$). The estimated volume ($V = 208702 \text{ \AA}^3$) was deduced from the measured diffusion coefficient ($D = 1.10 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$).

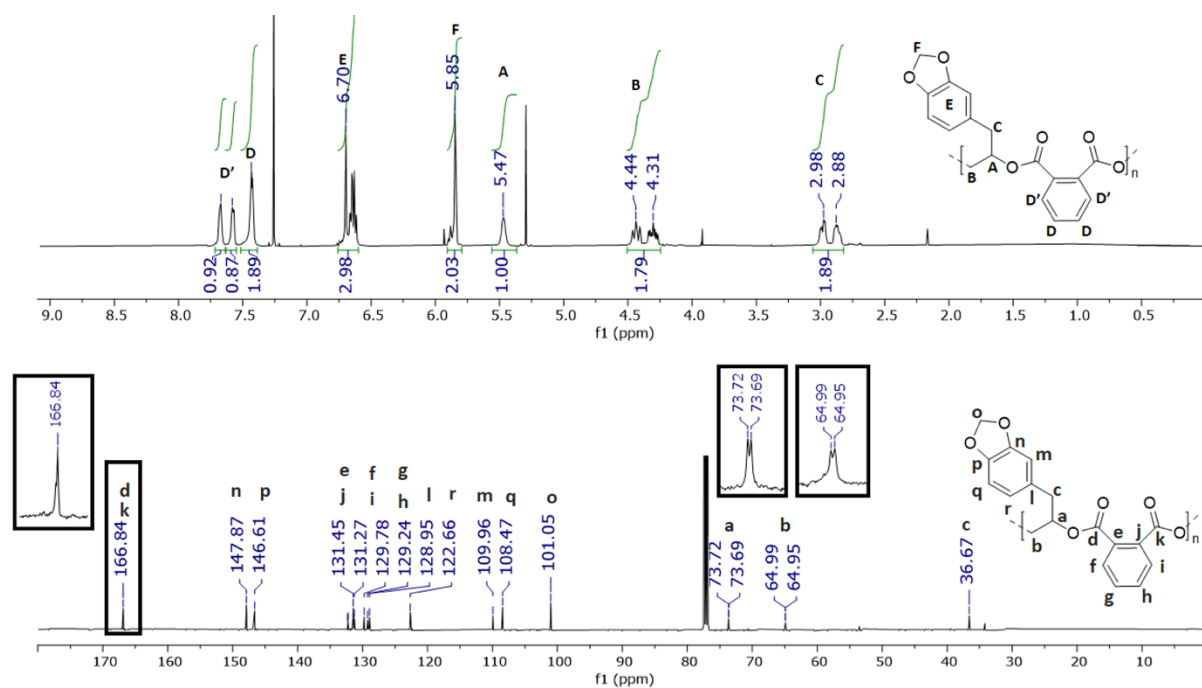


Figure S27. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz, CDCl_3) of isolated p(PA-*alt*-SO) formed from the ROCOP of PA and SO initiated by IPr. Conditions: 250/300/1 (PA/CHO/IPr), no solvent, 90 °C, 16 h (100 % conversion of PA).

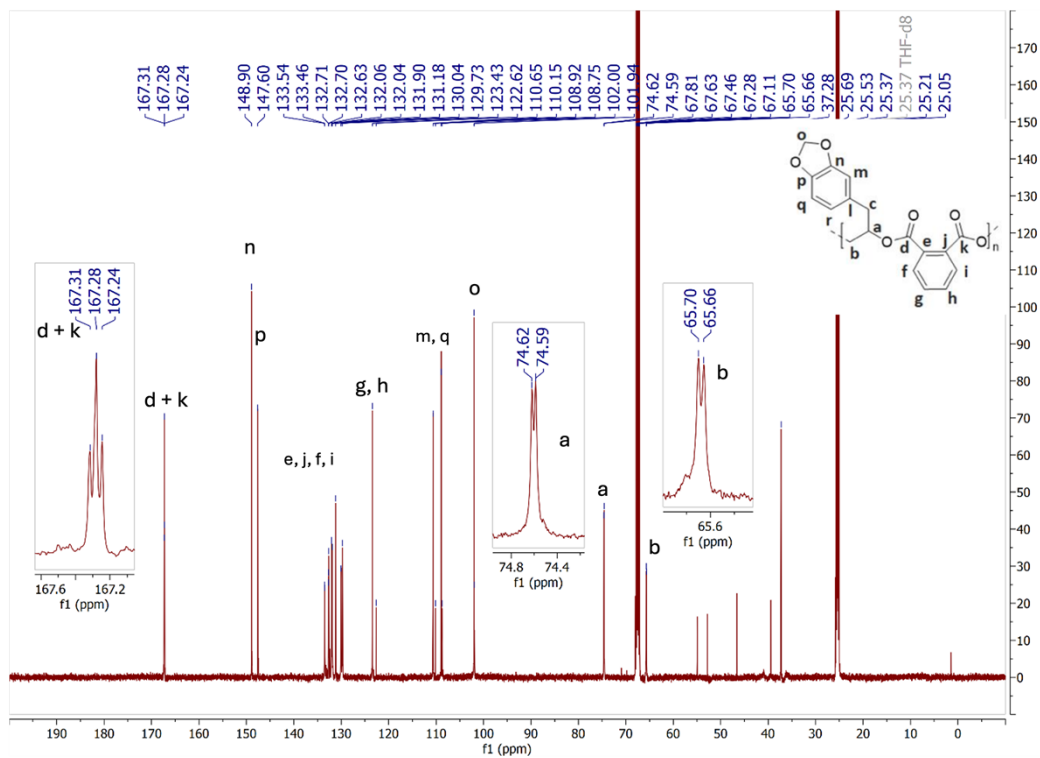


Figure S28. ¹³C NMR (125 MHz, THF-d⁸) spectrum of poly(PA-*alt*-SO).

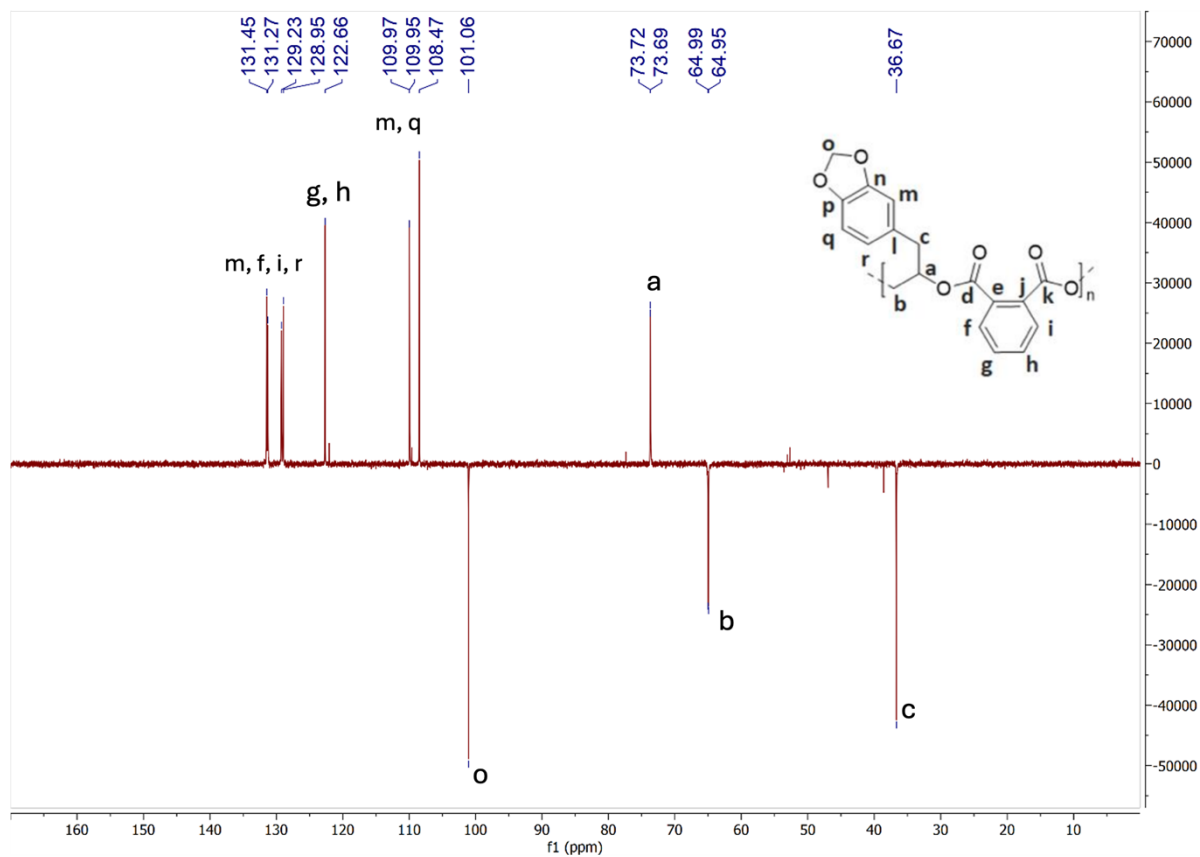


Figure S29. DEPT 135 NMR (125 MHz, CDCl₃) spectrum of poly(PA-*alt*-SO).

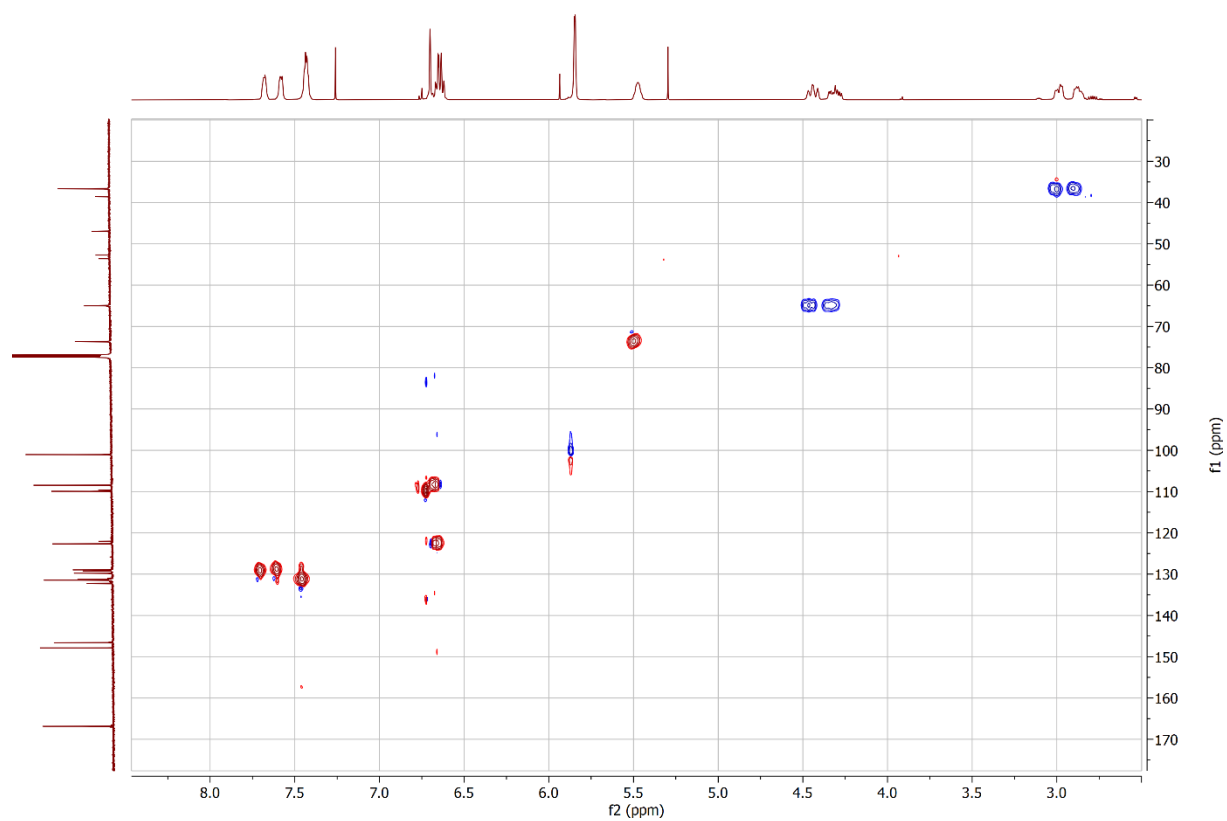


Figure S30. HSQC NMR (500 MHz, 125 MHz, CDCl₃) spectrum of poly(PA-*alt*-SO).

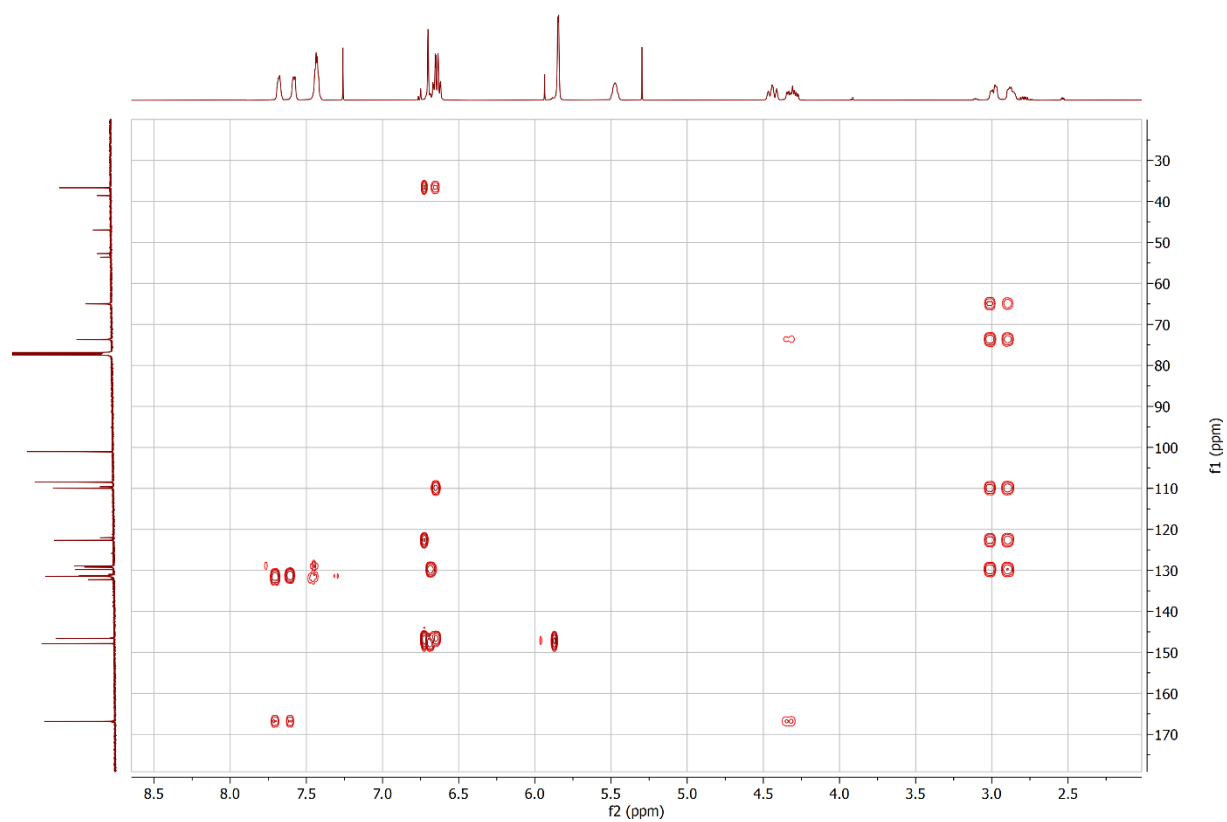


Figure S31. HMBC NMR (500 MHz, 125 MHz, CDCl₃) spectrum of poly(PA-*alt*-SO).

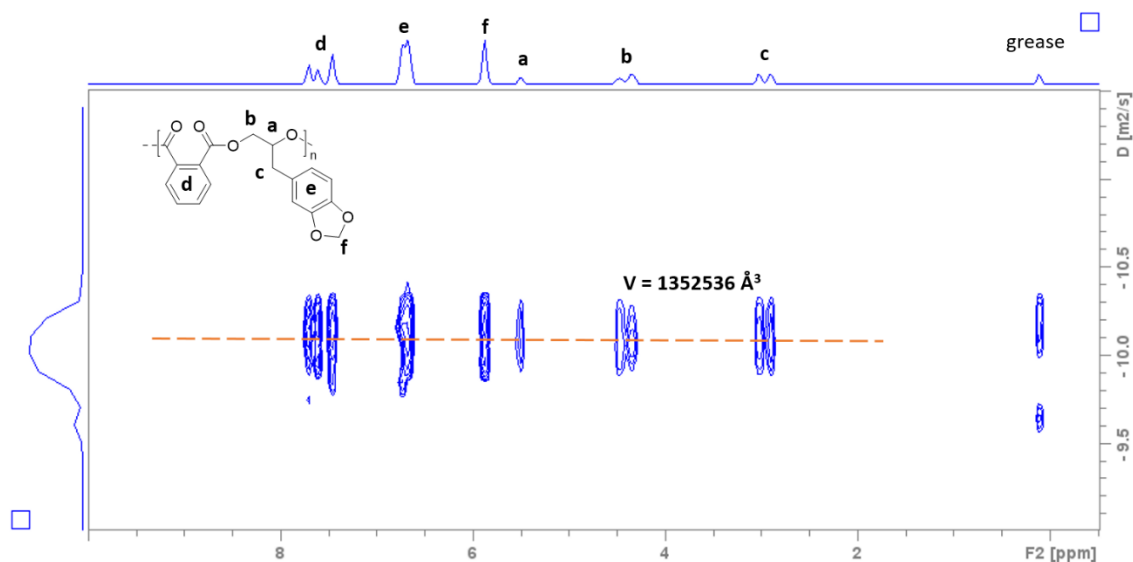


Figure S32. ^1H DOSY NMR (CDCl_3 , 600 MHz) of isolated poly(PA-*alt*-SO) formed from the ROCOP of PA and SO initiated by IPr (PA/SO/IPr (250/300/1), 90 °C, 16 h, 85% conversion of PA, $M_n \text{ GPC} = 45.3 \text{ kg mol}^{-1}$, $D = 1.39$). The estimated volume ($V = 1352536 \text{ \AA}^3$) was deduced from the measured diffusion coefficient ($D = 5.90 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$).

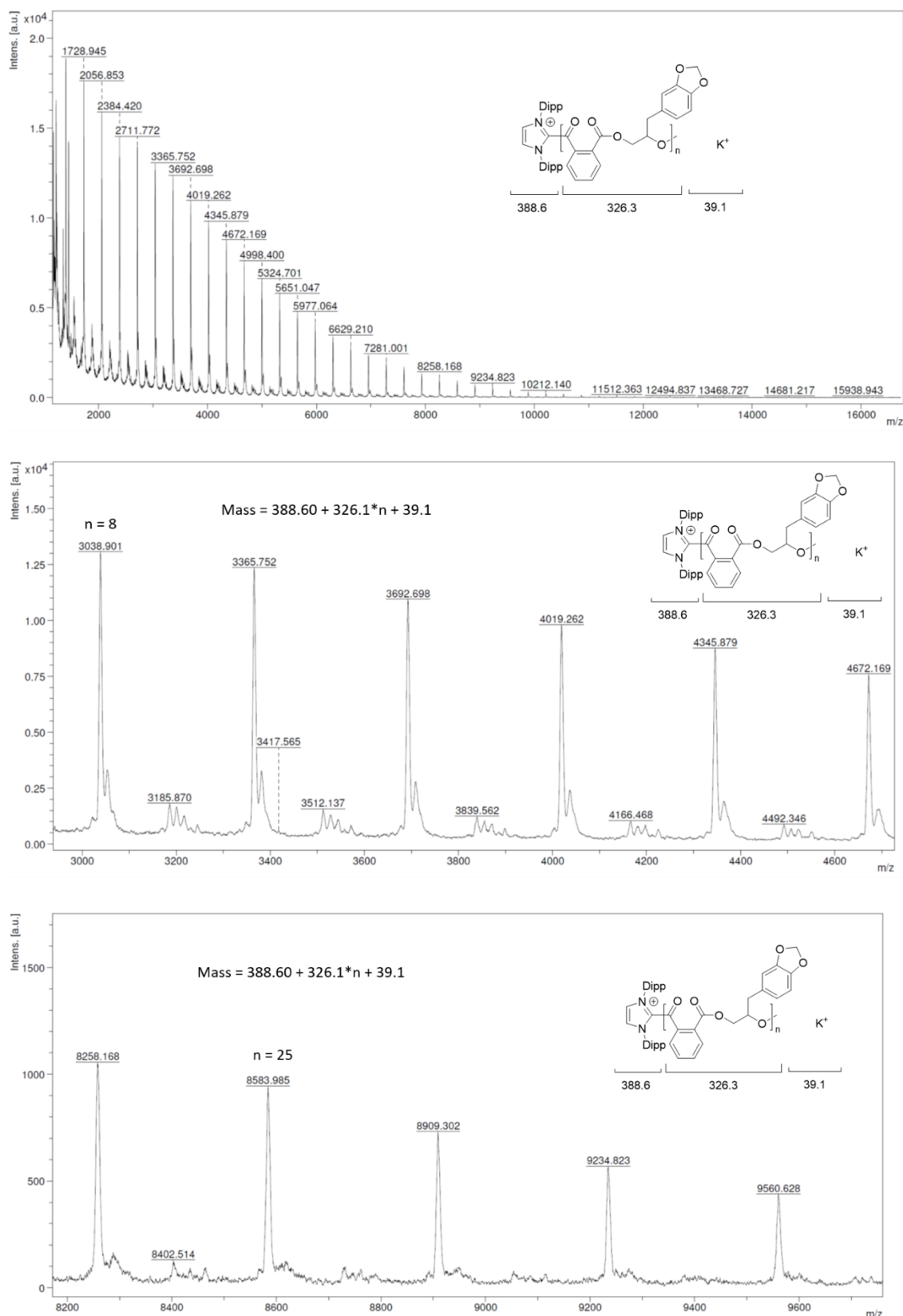
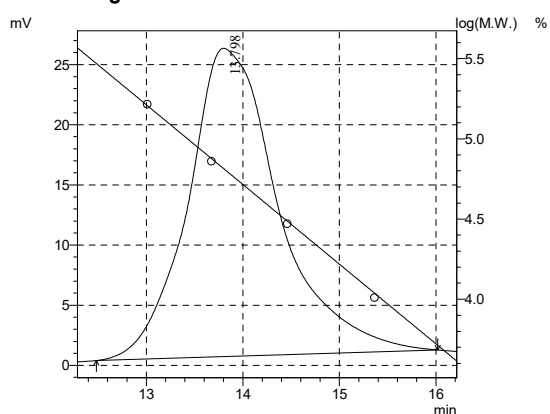


Figure S33. MALDI-TOF mass spectra (including the full spectrum and two zooms: top, central and bottom spectrum, respectively) for isolated p(PA-*alt*-SO) formed from the ROCOP of PA and SO initiated by IPr. Conditions: 20/25/1 (PA/SO/IPr), no solvent, 90 °C, 6 h (> 95 % conversion of PA).

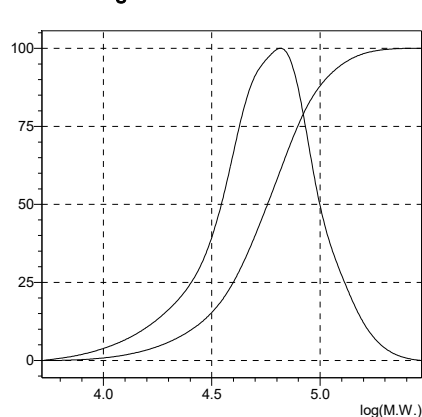
==== Shimadzu LCsolution GPC Analysis Report ====

Acquired by : Admin
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 Sample ID : AS059 crude
 Vial# :
 Injection Volume : 100 uL
 Data Filename : AS059 crude.lcd
 Method Filename : gpc.lcm
 Batch Filename :
 Report Filename : Report_template.lcr
 Date Acquired : 24/05/2024 16:42:15
 Data Processed : 24/05/2024 17:07:18

Chromatogram & Calibration Curve



Molecular Weight Distribution Curve



GPC Calculation Results

Peak#:1 (Detector A Ch1)

[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	12.483	12.483	295095	400
Top	13.798	13.798	65516	25635
End	16.017	16.017	5164	1276

Area : 1676352

Area% : 100.0000

[Average Molecular Weight]

Number Average Molecular Weight(Mn)	45273
Weight Average Molecular Weight(Mw)	63067
Z Average Molecular Weight(Mz)	81330
Z+1 Average Molecular Weight(Mz1)	101162
Mw/Mn	1.39303
Mv/Mn	1.34106
Mz/Mw	1.28959

Detector A Ch1

[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	45273
Weight Average Molecular Weight(Mw)	63067
Z Average Molecular Weight(Mz)	81330
Z+1 Average Molecular Weight(Mz1)	101162
Mw/Mn	1.39303
Mv/Mn	1.34106
Mz/Mw	1.28959

C:\LabSolutions\Data\Antoine\DonnUes\AS059 crude.lcd

Figure S34. GPC traces of crude p(PA-*alt*-SO) produced from the ROCOP of PA and SO initiated by IPr. Conditions: 250/300/1 (PA/SO/IPr), no solvent, 90 °C, 16 h (85 % conversion of PA).

DSC data

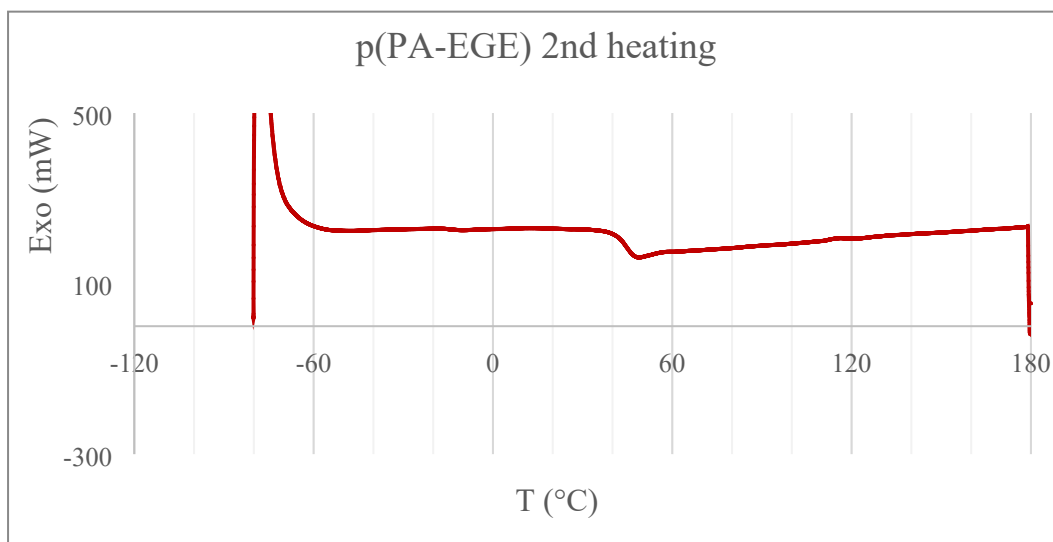


Figure S35. DSC thermogram for an isolated p(PA-*alt*-EGE) material ($M_n = 12.1 \text{ kg}\cdot\text{mol}^{-1}$, $\bar{D} = 1.20$). Sweeping rate: $10 \text{ }^\circ\text{C}$ per minute. Only the second heating process is depicted and is in line with an amorphous material ($T_g = 44 \text{ }^\circ\text{C}$).

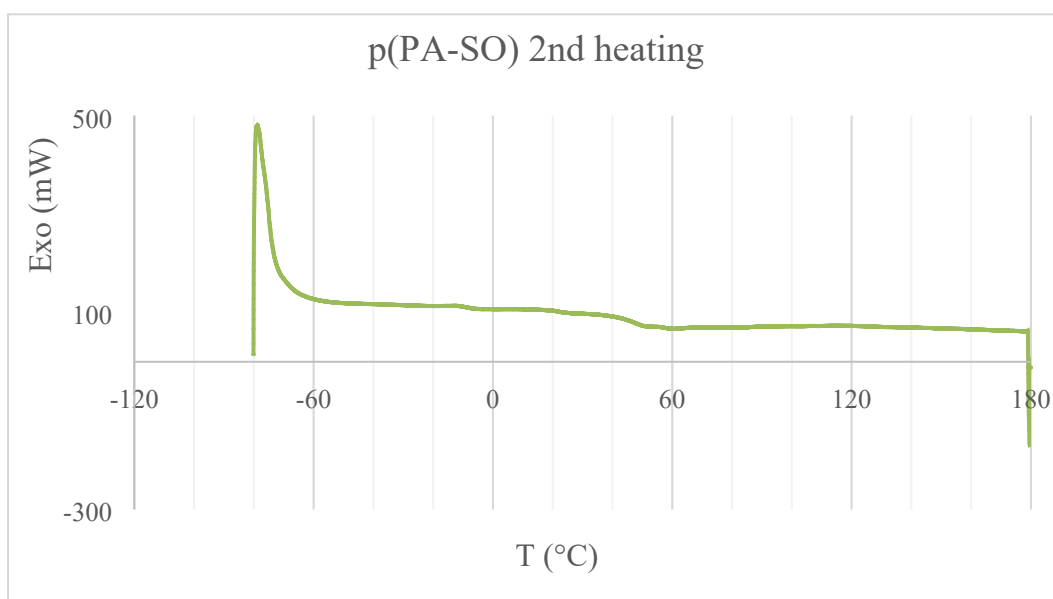


Figure S36. DSC thermogram for an isolated p(PA-*alt*-EGE) material ($M_n = 45.3 \text{ kg}\cdot\text{mol}^{-1}$, $\bar{D} = 1.39$). Sweeping rate: $10 \text{ }^\circ\text{C}$ per minute. Only the second heating process is shown and is in line with an amorphous material ($T_g = 48 \text{ }^\circ\text{C}$).

DFT Computational details

All calculations were performed with GAUSSIAN 16 (version C01) at DFT level (functional ω B97XD).⁹ All atoms were described by Pople bases 6-31+G**.¹⁰ Calculations were performed in THF to model solvation by epoxide. All structures were optimized and the nature of the met stationary point determined by frequency calculation. Minima are characterized by a set of real frequencies and transition states by an imaginary frequency. The free energy was extracted from this frequency calculation. The origin of the energies is constituted by the separate fragments.

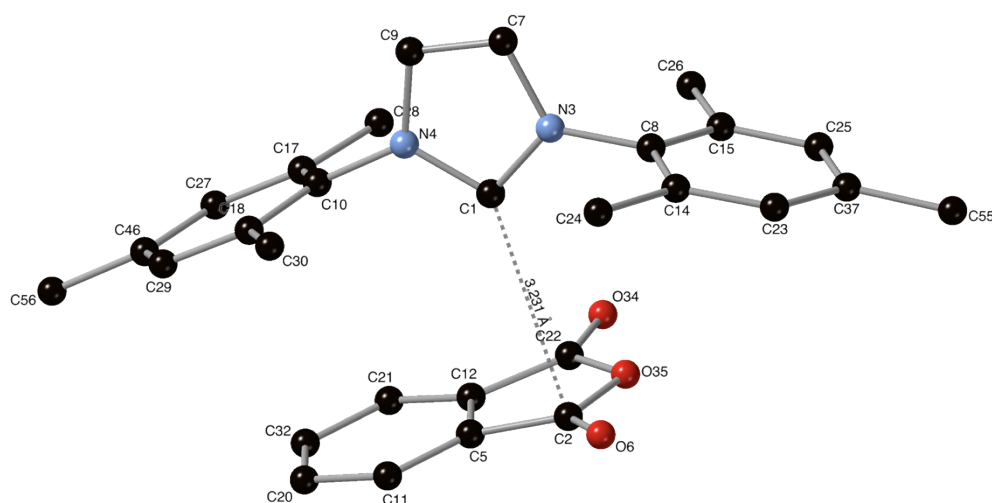


Figure S37. Molecular structure of reactant complex associating a model of IMes (A) and a PA model (B).

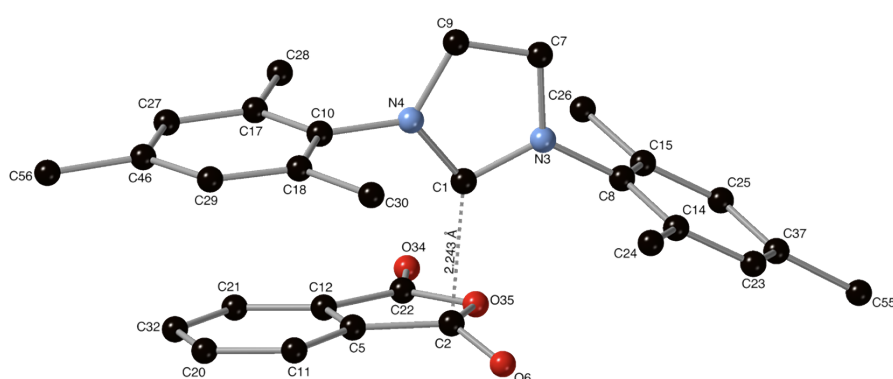


Figure S38. Molecular structure of transition state TS resulting from the nucleophilic attack of B by A.

⁹ J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.*, **2008**, *10*, 6615.

¹⁰ R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.*, **1971**, *54*, 724.

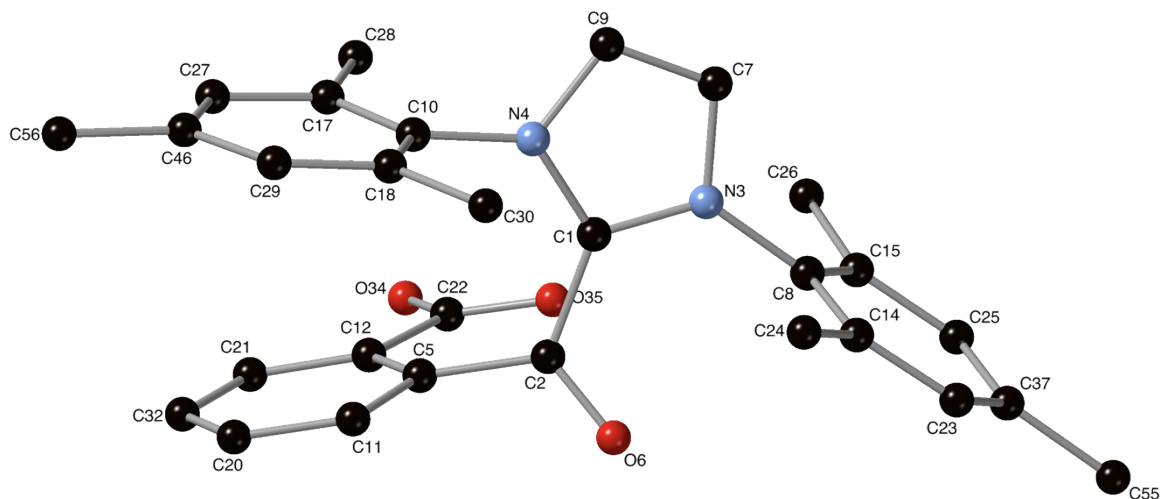


Figure S39. Molecular structure of the ring-opened model product **D**.

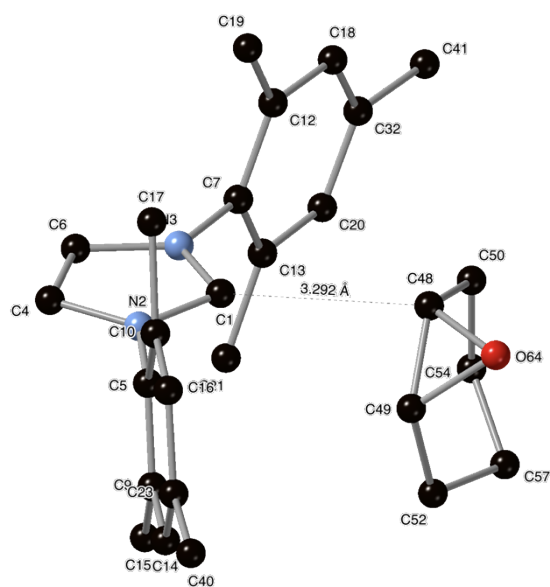


Figure S40. Molecular structure of reactant complex associating a model of IMes (**A**) and a CHO model (**C**).

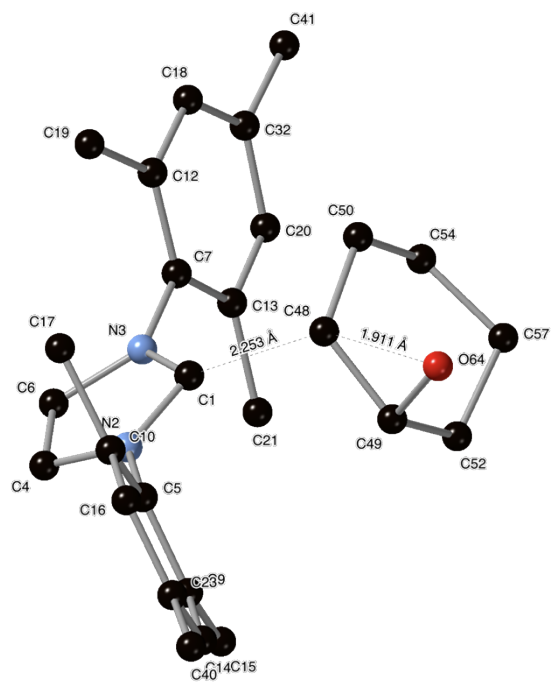


Figure S41. Molecular structure of transition state TS' resulting from the nucleophilic attack of C by A.

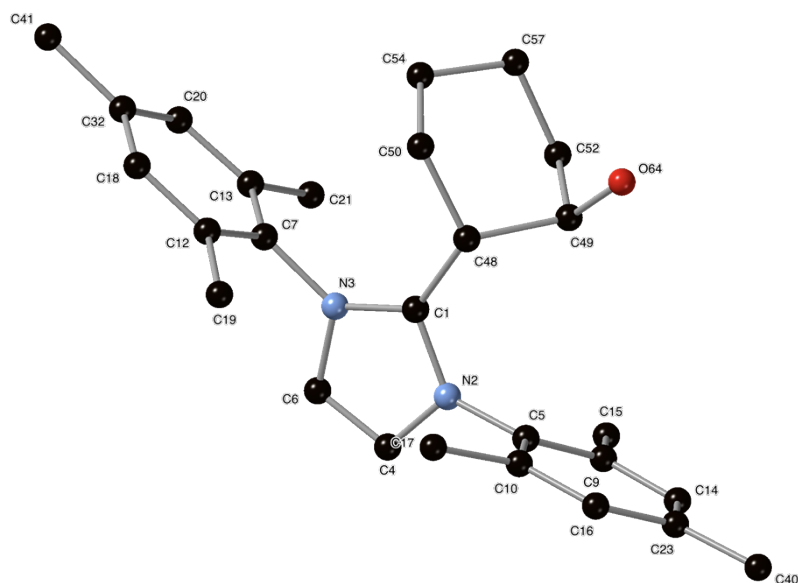


Figure S42. Molecular structure of the ring-opened model product E.