

# Dr Étienne Grau



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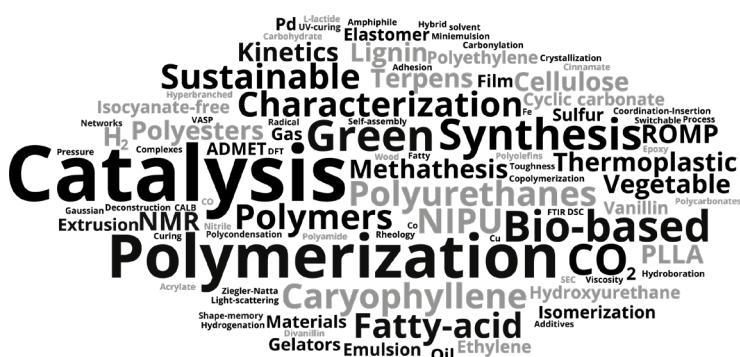
## ASSISTANT PROFESSOR

My expertise is in **polymer chemistry** and **catalysis**. In the last 7 years, I developed **green chemistry approaches to bio-based polymers**.

I focus my research topics on the valorization of biomass and more specifically on the **synthesis of fatty-acid based thermoplastic polymers**. To do so, fatty acids are modified using green chemistry methodologies (catalysis, green solvent, atom efficient reaction...) to obtain polymerizable synthons. More recently, this approach was broadened to other bio-resources such as terpenes or lignin derivates.

I manage a platform of equipments for **chemistry under high pressure** (ethylene, propylene, CO<sub>2</sub>, H<sub>2</sub>, ...). The related research topics concern the polymer foaming by supercritical CO<sub>2</sub>, the polymerization in CO<sub>2</sub>, coordination-insertion polymerization of ethylene and chemical valorization of CO<sub>2</sub>.

### EXPERTISE



### OTHERS SKILLS

Proactive  
Management  
Communication  
Leadership  
Teaching

French

English



### PROFESSIONAL EXPERIENCE

- 2013-present **University of Bordeaux – France**  
Assistant Professor in *Biopolymers and Bio-Sourced Polymers* team (team leader: Pr. H. Cramail), LCPO
- Published 61 research articles and 8 patents
  - Supervised 12 PhD students and 4 Post-doc
  - Coordinated 7 projects
  - Manage a professional bachelor on polymer formulation
  - Part of the UB chemistry bachelor board
  - Part of Double Master in Polymer Science board
  - Editor-in-Chief of [Green Materials](#)
  - Part of the organization committee of BPC2018 and JEPO19
  - Chair of the Frontier in Green Material Symposia
  - Create and organize a webinar series on Polymer Science



### 2012-2013 Konstanz University – Germany

Post-doc researcher

*Application of Pd Catalysis to Terpenes*

Supervisor: Pr. Dr. S. Mecking

### 2010-2012 ETH Zurich – Switzerland

Post-doc researcher in collaboration with ENS Lyon and C2P2 laboratory

*Ethylene Polymerization by Ziegler-Natta Catalysis*

Supervisor: Pr. Dr. C. Copéret and Pr. Dr. P. Sautet

### EDUCATION & TRAINING

#### 2007-2010

#### PhD in Chemistry

*Homo- and co-polymerization of ethylene via radical and/or catalytic pathways*

C2P2 Laboratory – University of Lyon

Doctoral Fellowship

Supervisor: Dr. C. Boisson and Dr. V. Monteil



#### 2003-2007

#### Bachelor of Science in Physico-Chemistry with a specialization in Polymers Science

ENS Cachan

### HOBBIES



Cooking



DIY



BJJ



Games

## PUBLICATIONS

### JOURNAL ARTICLES :



1. Grau, E.; Broyer, J.-P.; Boisson, C.; Spitz, R. & Monteil, V. "Free Ethylene Radical Polymerization under Mild Conditions: The Solvent Impact" *Macromolecules*, **2009**, *42*, 7279-7281
2. Grau, E.; Broyer, J.-P.; Boisson, C.; Spitz, R. & Monteil, V. "Supercritical Behavior in Free Radical Polymerization of Ethylene in the Medium Pressure Range" *Physical Chemistry Chemical Physics*, **2010**, *12*, 11665-11669.
3. Grau, E.; Dugas, P.-Y.; Broyer, J.-P.; Boisson, C.; Spitz, R. & Monteil, V. "Aqueous Dispersions of Non Spherical Polyethylene Nanoparticles from Free Radical Polymerization under mild conditions" *Angew. Chem. Int. Ed.*, **2010**, *49*, 6810-6812
4. Chitta, R.; Brüll, R.; Macko, T.; Monteil, V.; Boisson, C.; Grau, E. & Leblanc, A. "Characterization of ethylene-methylmethacrylate and ethylene-butylacrylate copolymers with interactive liquid chromatography" *Macromol. Symp.*, **2010**, *298*, 191-199
5. Leblanc, A.; Grau, E.; Broyer, J.-P.; Boisson, C.; Spitz, R. & Monteil, V. "Homo-and copolymerizations of (meth)acrylates with olefins (styrene, ethylene) using neutral nickel complexes: a dual radical/catalytic pathway" *Macromolecules*, **2011**, *44*, 3293-3301
6. Grau, E.; Broyer, J.-P.; Boisson, C.; Spitz, R. & Monteil, V. "Unusual activation by solvent of the ethylene free radical polymerization" *Polymer Chemistry*, **2011**, *2*, 2328-2333
7. Grau, E.; Lesage, A.; Norsic, S.; Copéret, C.; Monteil, V. & Sautet, P. "Tetrahydrofuran in TiCl<sub>4</sub>/THF/MgCl<sub>2</sub>: a Non-Innocent Ligand for Supported Ziegler-Natta Polymerization Catalysts" *ACS Catalysis*, **2013**, *3*, 52-56
8. Grau, E. & Mecking, S. "Polyterpenes by ring opening metathesis polymerization of caryophyllene and humulene" *Green Chemistry*, **2013**, *15*, 1112-1115
9. Maisonneuve, L.; Lebarb  , T.; Grau, E. & Cramail, H. "Structure--properties relationship of fatty acid-based thermoplastics as synthetic polymer mimics" *Polymer Chemistry*, **2013**, *4*, 5472-5517
10. Lebarb  , T.; More, A. S.; Sane, P. S.; Grau, E.; Alfos, C. & Cramail, H. "Bio-Based Aliphatic Polyurethanes Through ADMET Polymerization in Bulk and Green Solvent" *Macromolecular rapid communications*, **2014**, *35*, 479-483
11. Lebarb  , T.; Neqal, M.; Grau, E.; Alfos, C. & Cramail, H. "Branched polyethylene mimicry by metathesis copolymerization of fatty acid-based  $\alpha$ ,  $\omega$ -dienes" *Green Chemistry*, **2014**, *16*, 1755-1758
12. Estevez, Y.; Gardrat, C.; Berthelot, K.; Grau, E.; De Jeso, B.; Ouardad, S. & Peruch, F. "Unexpected dimerization of isoprene in a gas chromatography inlet. A study by gas chromatography/mass spectrometry coupling" *Journal of Chromatography A*, **2014**, *1331*, 133-138
13. Maisonneuve, L.; More, A. S.; Foltran, S.; Alfos, C.; Robert, F.; Landais, Y.; Tassaing, T.; Grau, E. & Cramail, H. "Novel green fatty acid-based bis-cyclic carbonates for the synthesis of isocyanate-free poly (hydroxyurethane amide)s" *RSC Advances*, **2014**, *4*, 25795-25803
14. Maisonneuve, L.; Wirotius, A.-L.; Alfos, C.; Grau, E. & Cramail, H. "Fatty acid-based (bis) 6-membered cyclic carbonates as efficient isocyanate free poly (hydroxyurethane) precursors" *Polymer Chemistry*, **2014**, *5*, 6142-6147
15. Busch, H.; Stempfle, F.; He  , S.; Grau, E. & Mecking, S. "Selective isomerization--carbonylation of a terpene trisubstituted double bond" *Green Chemistry*, **2014**, *16*, 4541-4545
16. Lebarb  , T.; Alfos, C.; Gadenne, B.; Grau, E. & Cramail, H. "Synthesis of Fatty acid-based polyesters and their blends with Poly (L-Lactide) as a way to tailor PLLA toughness" *ACS Sustainable Chemistry & Engineering*, **2014**, *3*, 283-292
17. Rix, E.; Ceglia, G.; Bajt, J.; Chollet, G.; Heroguez, V.; Grau, E. & Cramail, H. "Hydrophobe-free miniemulsion polymerization: towards high solid content of fatty acid-based poly (urethane-urea) latexes" *Polymer Chemistry*, **2015**, *6*, 213-217
18. Llevot, A.; Grau, E.; Carlotti, S.; Grelier, S. & Cramail, H. "Dimerization of abietic acid for the design of renewable polymers by ADMET" *European Polymer Journal*, **2015**, *67*, 409-417
19. Lebarb  , T.; Grau, E.; Alfos, C. & Cramail, H. "Fatty acid-based thermoplastic poly (ester-amide) as toughening and crystallization improver of poly (l-lactide)" *European Polymer Journal*, **2015**, *65*, 276-285
20. Llevot, A.; Grau, E.; Carlotti, S.; Grelier, S. & Cramail, H. "Renewable (semi) aromatic polyesters from symmetrical vanillin-based dimers" *Polymer Chemistry*, **2015**, *6*, 6058-6066
21. Ho  st  lek, Z.; Mundil, R.; C  sa  rov  , I.; Trhl  k  ov  , O.; Grau, E.; Peruch, F.; Cramail, H. & Merna, J. "Salphen-Co (III) complexes catalyzed copolymerization of epoxides with CO<sub>2</sub>" *Polymer*, **2015**, *63*, 52-61
22. Llevot, A.; Grau, E.; Carlotti, S.; Grelier, S. & Cramail, H. "ADMET polymerization of bio-based biphenyl compounds" *Polymer Chemistry*, **2015**, *6*, 7693-7700
23. Maisonneuve, L.; Lamarzelle, O.; Rix, E.; Grau, E. & Cramail H. "Isocyanate-Free Routes to Polyurethanes and Poly (hydroxy Urethane)s" *Chemical Reviews*, **2015**, *115*, 12407-12439
24. Llevot, A.; Grau, E.; Carlotti, S.; Grelier, S. & Cramail, H. "From Lignin-derived Aromatic Compounds to Novel Biobased Polymers" *Macromolecular rapid communications*, **2016**, *37*, 9-28
25. Llevot, A.; Grau, E.; Carlotti, S.; Grelier, S. & Cramail, H. "Selective laccase-catalyzed dimerization of phenolic compounds derived from lignin: Towards original symmetrical bio-based (bis) aromatic monomers" *Journal of Molecular Catalysis B: Enzymatic*, **2016**, *125*, 34-41
26. Maisonneuve, L.; Chollet, G.; Grau, E. & Cramail, H. "Vegetable oils: a source of polyols for polyurethane materials" *OCL*, **2016**, *23*, D508
27. Sane, P.; Lebarb  , T.; Grau, E. & Cramail, H. "Isomerization-Hydroboration-Oxidation Strategy: Access to Long Chain AB-and AA-type Oleyl Based Monomers and Polymers Thereof" *European Journal of Lipid Science and Technology*, **2016**, *118*, 1620-1629

28. Hibert, G.; Lamarzelle, O.; Maisonneuve, L.; Grau, E. & Cramail, H. "Bio-based aliphatic primary amines from alcohols through the 'Nitrile route'towards non-isocyanate polyurethanes" *European Polymer Journal*, **2016**, 82, 114-121
29. Lamarzelle, O.; Durand, P.L.; Wirotius, A.L.; Chollet, G.; Grau, E. & Cramail H. "Activated lipidic cyclic carbonates for non-isocyanate polyurethane synthesis" *Polymer Chemistry*, **2016**, 7, 1439-1451. Lamarzelle, O.; Durand, P.L.; Wirotius, A.L.; Chollet, G.; Grau, E. & Cramail H. "Activated lipidic cyclic carbonates for non-isocyanate polyurethane synthesis" *Polymer Chemistry*, **2016**, 7, 1439-1451.
30. Rix, E.; Chollet, G.; Grau, E. & Cramail, H. "Synthesis of fatty acid-based non-isocyanate polyurethanes, NIPUs, in bulk and mini-emulsion" *European Polymer Journal*, **2016**, 84, 863-872
31. Testud, B. ; Pintori, D.; Grau, E.; Taton, D. & Cramail, H. "Hyperbranched polyesters by polycondensation of fatty acid-based AB n-type monomers" *Green Chemistry*, **2017**, 19, 259-269
32. Over, L.C.; Grau, E.; Grelier, S.; Meier, M.A.R. & Cramail, H. "Synthesis and Characterization of Epoxy Thermosetting Polymers from Glycidylated Organosolv Lignin and Bisphenol A" *Macromolecular Chemistry and Physics*, **2017** , 218, 1600411
33. Lamarzelle, O.; Hibert, G.; Lecommandoux, S.; Grau, E. & Cramail, H. "A thioglycerol route to bio-based bis-cyclic carbonates: poly (hydroxyurethane) preparation and post-functionalization" *Polymer Chemistry*, **2017**, 8 , 3438-3447
34. Hibert, G.; Grau, E.; Pintori, D.; Lecommandoux, S.& Cramail H. "ADMET polymerization of  $\alpha$ ,  $\omega$ -unsaturated glycolipids: synthesis and physico-chemical properties of the resulting polymers" *Polymer Chemistry* **2018**, 8 (24), 3731-3739
35. Onwukamike, K.N.; Tassaing, T.; Grelier, S.; Grau, E.; Cramail, H. & Meier M.A.R. "Detailed understanding of the DBU/CO<sub>2</sub> switchable solvent system for cellulose solubilization and derivatization" *ACS Sustainable Chemistry & Engineering*, **2017**, 6 (1), 1496-1503
36. Dubois, J.; Grau, E.; Tassaing, T. & Dumon M. "On the CO<sub>2</sub> sorption and swelling of elastomers by supercritical CO<sub>2</sub> as studied by in situ high pressure FTIR microscopy" *The Journal of Supercritical Fluids*, **2018**, 131, 150-156
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38. Durand, P.L.; Brège, A.; Chollet, G.; Grau, E. & Cramail H. "Simple and Efficient Approach toward Photosensitive Biobased Aliphatic Polycarbonate Materials" *ACS Macro Letters*, **2018**, 7 (2), 250-254
39. Bonnot, L.; Len, C.; Grau, E. & Cramail H. "Divinylglycol, a Glycerol-Based Monomer: Valorization, Properties, and Applications" *Green Polymer Chemistry: New Products, Processes, and Applications*, **2018**, 299-330
40. Onwukamike, K.N.; Grelier, S.; Grau, E.; Cramail, H. & Meier M.A.R. "Sustainable Transesterification of Cellulose with high oleic sunflower oil in a DBU-CO<sub>2</sub> Switchable Solvent" *ACS Sustainable Chemistry & Engineering*, **2018**, 6 (7), 8826-8835
41. Arcens, D.; Grau, E.; Cramail, H. & Peruch, F. "6-O-glucose palmitate synthesis with lipase: Investigation of some key parameters" *Molecular Catalysis*, **2018**, 460, 63-68
42. Kuhire, S.S.; Ichake, A.B.; Grau, E.; Cramail, H. & Wadgaonkar P.P. "Synthesis and Characterization of Partially Bio-Based Polyimides Based on Biphenylene-Containing Diisocyanate Derived from Vanillic Acid" *European Polymer Journal*, **2018**, 109, 257-264
43. Bossion, A.; Aguirresarobe, R.H.; Irusta, L.; Taton, D.; Cramail, H.; Grau, E.; Mecerreyes, D.; Su, C.; Liu, G.; Müller, A.J. & Sardon H. "Unexpected Synthesis of Segmented Poly (hydroxyurea–urethane)s from Dicyclic Carbonates and Diamines by Organocatalysis" *Macromolecules*, **2018**, 51 (15), 5556-5566
44. Savonnet, E.; Grau, E.; Defoort, B. & Cramail H. "Divanillin-Based Epoxy Precursors as DGEBA Substitutes for Biobased Epoxy Thermosets" *ACS Sustainable Chemistry & Engineering*, **2018**, 6 (8), 11008-11017
45. Onwukamike, K.N.; Grelier, S.; Grau, E.; Cramail, H. & Meier M.A.R. "On the direct use of CO<sub>2</sub> in multicomponent reactions: introducing the Passerini four component reaction" *RSC Advances*, **2018**, 8 (55), 31490-31495
46. Pawar, G.G.; Robert, F.; Grau, E.; Cramail, H. & Landais, Y. "Visible-light photocatalyzed oxidative decarboxylation of oxamic acids: a green route to urethanes and ureas" *Chemical Communications*, **2018**, 54 (67), 9337-9340
47. Rosselgong, J.; Chemin, M.; Almada, C.C.; Hemery, G.; Guigner, J.M.; Chollet, G.; Labat, G.; Da Silva Perez, D.; Ham-Pichavant, F.; Grau, E.; Grelier, S.; Lecommandoux, S. & Cramail H. "Synthesis and self-assembly of Xylan-based amphiphiles: from bio-based vesicles to antifungal properties" *Biomacromolecules*, **2018**, 20 (1), 118-129
48. Onwukamike, K.N.; Grelier, S.; Grau, E.; Cramail, H. & Meier M.A.R. "Critical Review on Sustainable Homogeneous Cellulose Modification: Why Renewability Is Not Enough" *ACS Sustainable Chemistry & Engineering*, **2018**, 7 (2), 1826-1840
49. Durand, P.L.; Chollet, G.; Grau, E. & Cramail H. "Versatile cross-linked fatty acid-based polycarbonate networks obtained by thiol–ene coupling reaction" *RSC Advances*, **2019**, 9 (1), 145-150
50. Hibert, G.; Fauquignon, M.; Le Meins, J.F.; Pintori, D.; Grau, E.; Lecommandoux, S. & Cramail H. "Organogels from trehalose difatty ester amphiphiles" *Soft Matter*, **2019**, 15 (5), 956-962
51. Onwukamike, K.N.; Lapuyade, L.; Maille, L.; Grelier, S.; Grau, E.; Cramail, H. & Meier M.A.R. "Sustainable approach for Cellulose aerogel preparation from the DBU-CO<sub>2</sub> Switchable Solvent" *ACS Sustainable Chemistry & Engineering*, **2019**, 7 (3), 3329-3338
52. Savonnet, E.; Grau, E.; Grelier, S.; Defoort, B. & Cramail H. "Divanillin-based aromatic amines: synthesis and use as curing agents for fully vanillin-based epoxy thermosets" *Frontiers in Chemistry*, **2019**, 7:606
53. Pessoni, L.; Sane, P.; Grau, E. & Cramail, H. "Cationic water dispersion of bio-sourced cross-linked polyurethane" *Green Materials*, **2019**, 7 (4), 185-193
54. Magliozzi, F.; Chollet, G.; Grau, E. & Cramail, H. "Benefit of the Reactive Extrusion in the Course of Polyhydroxyurethanes Synthesis by Aminolysis of Cyclic Carbonates" *ACS Sustainable Chemistry & Engineering*, **2019**, 7 (20), 17282-17292

55. Dworakowska, S.; Le Coz, C.; Grau, E. & Cramail, H. "Cross-Linking of Polyesters Based on Fatty Acids" *European Journal of Lipid Science and Technology*, **2019**, 121 (11), 1900264
56. Durand, P.L.; Grau, E. & Cramail H. "Bio-Based Thermo-Reversible Aliphatic Polycarbonate Network" *Molecules*, **2020**, 25 (1), 74
57. Medeiros, A.M.M.S. & Grau E. "Caryophyllene as a precursor of cross-linked materials", *ACS Sustainable Chemistry & Engineering*, **2020**, 8 (11), 4451-4456
58. Arcens, D.; Grau, E.; Grelier, S.; Cramail, H. & Peruch, F. "Impact of Fatty Acid Structure on CALB-Catalyzed Esterification of Glucose" *European Journal of Lipid Science and Technology*, **2020**, 122 (4), 1900294
59. Garbay, G.; Giraud, L.; Gali, S.M.; Hadzioannou, G.; Grau, E.; Grelier, S.; Cloutet, E.; Cramail, H. & Brochon, C. "Divanillin-Based Polyazomethines: Toward Biobased and Metal-Free  $\pi$ -Conjugated Polymers" *ACS Omega*, **2020**, 5 (10), 5176-5181
60. Bizet, B.; Grau, E.; Cramail, H. & Asua, J.M. "Water-based Non-Isocyanate Polyurethanes-Polyureas (NIPUUs)" *Polymer Chemistry*, **2020**, DOI: 10.1039/D0PY00427H
61. Maglizzi, F.; Scali, A.; Chollet, G.; Montarnal, D.; Grau, E. & Cramail, H. "Hydrolyzable Biobased Polyhydroxyurethane Networks with Shape Memory Behavior at Body Temperature" *ACS Sustainable Chemistry & Engineering*, **2020**, DOI: 10.1021/acssuschemeng.0c02610

## PATENTS :

1. Procédé de synthèse de copolymères à blocs comprenant des monomères vinyliques polaires et apolaires, Monteil V.; Boisson C.; Spitz R.; Grau E.; Broyer J.-P., (2011) EP 12799557, WO 2013083783
2. Vegetable oils-based non isocyanate polyurethanes via 6-membered cyclic carbonates, Cramail, H.; Grau E.; Maisonneuve L.; Alfos C., (2013) EP 13306735.5
3. Vegetable oils-based non isocyanate polyurethanes via 5-membered cyclic carbonates, Cramail, H.; Grau E.; Maisonneuve L.; Alfos C., (2013) EP 13306736.3
4. Hyperbranched polyesters, Testud B.; Grau E.; Pintori D.; Taton D.; Cramail H., (2014) EP14306642.1
5. New phenolic polymers and preparation processes thereof, Llevot A.; Cramail H.; Carlotti S.; Grau E.; Grelier S., (2014) EP14306563.9
6. New process for preparing biphenyl compounds, Llevot A.; Cramail H.; Carlotti S.; Grau E.; Grelier S., (2014) EP14306566.2
7. Nouvelle résines epoxy, Savonnet E.; Cramail H.; Grau E.; Grelier S., (2017) FR1760451
8. Novel branched sulfur-containing polymers, Testud B.; Grau E.; Pintori D.; Taton D.; Cramail H., (2018) US Patent App. 15/770,307