Dr Étienne Grau

Laboratoire de Chimie des Polymères Organiques (LCPO)
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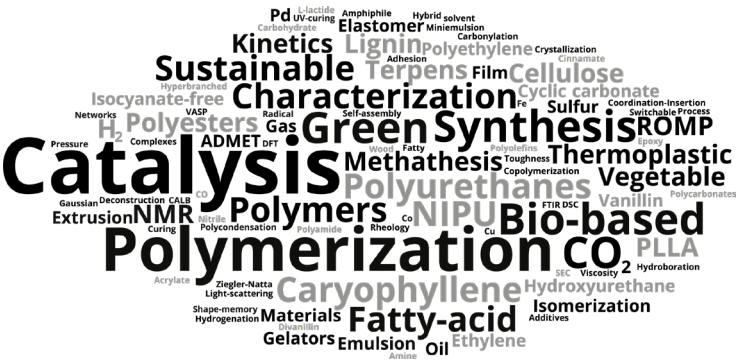
ASSISTANT PROFESSOR

My expertise is in **polymer chemistry** and **catalysis**. In the last 10 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_2, H_2, …). The related research topics concern the polymer foaming by supercritical CO_2, the polymerization in CO_2, coordination-insertion polymerization of ethylene and chemical valorization of CO_2.

Expertise



Others skills

Proactive
Management
Communication
Leadership
Teaching

French

English

Suite Office

Suite Adobe

Programming

Professional experience

2013-present **University of Bordeaux – France**
Assistant Professor in *Biopolymers and Bio-Sourced Polymers* team (team leader: Pr. H. Cramail), LCPO

- Published **82** research articles and **9** patents
- Supervised **13** PhD students and **4** Post-doc
- Coordinated **8** 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 2015-2019
- Part of the organization committee of BPC2018-2022 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 TiCl4/THF/MgCl2: 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.; Lebarbé, T.; Grau, E. & Cramail, H. "Structure--properties relationship of fatty acid-based thermoplastics as synthetic polymer mimics" *Polymer Chemistry,* **2013***, 4*, 5472-5517
10. Lebarbé, 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. Lebarbé, T.; Neqal, M.; Grau, E.; Alfos, C. & Cramail, H. "Branched polyethylene mimicry by metathesis copolymerization of fatty acid-based α, ω-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.; Heß, S.; Grau, E. & Mecking, S. "Selective isomerization--carbonylation of a terpene trisubstituted double bond" *Green Chemistry,* **2014***, 16*, 4541-4545
16. Lebarbé, 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. Lebarbé, 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. Hoštálek, Z.; Mundil, R.; Císařová, I.; Trhlíková, O.; Grau, E.; Peruch, F.; Cramail, H. & Merna, J. "Salphen-Co (III) complexes catalyzed copolymerization of epoxides with CO_2" *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.; Lebarbé, 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

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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.
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34. Onwukamike, K.N.; Tassaing, T.; Grelier, S.; Grau, E.; Cramail, H. & Meier M.A.R. "Detailed understanding of the DBU/CO2 switchable solvent system for cellulose solubilization and derivatization" *ACS Sustainable Chemistry & Engineering*, **2017,** 6 (1), 1496-1503
35. Hibert, G.; Grau, E.; Pintori, D.; Lecommandoux, S.& Cramail H. "ADMET polymerization of α, ω-unsaturated glycolipids: synthesis and physico-chemical properties of the resulting polymers" *Polymer Chemistry* **2018***,* 8 (24), 3731-3739
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39. 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-CO2 Switchable Solvent" *ACS Sustainable Chemistry & Engineering,* **2018***,* 6 (7), 8826–8835
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41. 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
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45. 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
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47. 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
48. 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
49. 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
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51. 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
52. Pessoni, L.; Sane, P.; Grau, E. & Cramail, H. "Cationic water dispersion of bio-sourced cross-linked polyurethane" *Green Materials,* **2019**, 7 (4), 185-193
53. 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
54. 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
55. Durand, P.L.; Grau, E. & Cramail H. "Bio-Based Thermo-Reversible Aliphatic Polycarbonate Network" *Molecules*, **2020**, 25 (1), 74

56. Medeiros, A.M.M.S. & Grau E. "Caryophyllene as a precursor of cross-linked materials", *ACS Sustainable Chemistry & Engineering*, **2020**, 8 (11), 4451-4456
57. 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
58. Garbay, G.; Giraud, L.; Gali, S.M.; Hadziioannou, G.; Grau, E.; Grelier, S.; Cloutet, E.; Cramail, H. & Brochon, C. "Divanillin-Based Polyazomethines: Toward Biobased and Metal-Free π-Conjugated Polymers" *ACS Omega*, **2020**, 5 (10), 5176-5181
59. Bizet, B.; Grau, E.; Cramail, H. & Asua, J.M. "Water-based Non-Isocyanate Polyurethanes-Polyureas (NIPUUs)" *Polymer Chemistry*, **2020**, *11*, 3786 - 3799
60. Magliozzi, 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**, *8*, 9125–9135
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67. Méheust, H.; Le Meins, J.F..; Grau, E. & Cramail, H. "Bio-Based Polyricinoleate and Polyhydroxystearate: Properties and Evaluation as Viscosity Modifiers for Lubricants" *ACS Applied Polymer Materials*, **2021**, *3*, 811-818
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69. Mehats, J.; Castets, L.; Grau, E. & Grelier, S. "Homogenization of Maritime Pine Wood Color by Alkaline Hydrogen Peroxide Treatment" *Coatings* **2021**, *11(7)*, 839
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BOOK CHAPTER :

1. Bonnot, L.; Len, C.; Grau, E. & Cramail H. “Divinylglycol, a Glycerol-Based Monomer: Valorization, Properties, and Applications” in Green Polymer Chemistry: New Products, Processes, and Applications, pp 299-330 (**2018**)
2. H. Cramail, B. Bizet, O. Lamarzelle, P-L. Durand, G. Hibert, E. Grau, "Bio-sourced Polymers: recent advances”, in World Scientific Publishing Company (WSPC) / Series on Chemistry, Energy and the Environment: Volume 6, Advanced Green Chemistry, Part 2 From catalysis to chemistry frontiers, https://doi.org/10.1142/11559 Chap 5 pp 167-328, Edited by Istvan T. Horvath and Max Malacria, (**2020**)
3. Durand, P.L.; Le Coz, C.; Grau, E. & Cramail H. “Fatty Acid-Based Polycarbonates Synthesis and Crosslinking through the Malonate Route” Sustainable Green Chemistry in Polymer Research. Volume 1. Biocatalysis and Biobased Materials pp 119-144 (**2023**)
4.

PATENTS :

1. “Method for synthesizing block copolymers including polar and non-polar vinyl monomers”, Monteil V.; Boisson C.; Spitz R.; Grau E.; Broyer J.-P., (2013) EP 12799557, WO 2013083783
2. “Six-membered cyclic biscarbonates for the preparation of polymers”, Cramail, H.; Grau E.; Maisonneuve L.; Alfos C., (2015) EP2883873A1
3. “Five-membered cyclic biscarbonates bearing amide linkages”, their preparation and their uses for the preparation of polymers, Cramail, H.; Grau E.; Maisonneuve L.; Alfos C., (2015) EP3083578A1
4. “New phenolic polymers and preparation processes thereof”, Llevot A.; Cramail H.; Carlotti S.; Grau E.; Grelier S., (2016) EP3002303A1
5. “Process for preparing biphenyl compounds”, Llevot A.; Cramail H.; Carlotti S.; Grau E.; Grelier S., (2016) EP3002333A1
6. “New branched polymers, their preparation process, and uses thereof”, Testud B.; Grau E.; Pintori D.; Taton D.; Cramail H., (2018) WO2018167201A1
7. “Novel branched sulfur-containing polymers”, Testud B.; Grau E.; Pintori D.; Taton D.; Cramail H., (2018) EP3368511A1
8. “Composes biphenyle pluriepoxydes, preparation et utilisations”, Savonnet E.; Cramail H.; Defoort B.; Grau E.; Grelier S., (2019) WO2019092359A1
9. “Composes biphenyle difonctionnels, preparation et utilisations”, Savonnet E.; Cramail H.; Defoort B.; Grau E.; Grelier S., (2019) WO2019155169A1

Diffusion du savoir

Interviews :

1. Combien de temps les masques mettent-ils à se décomposer?
   Huffington Post, 22 Mai 2020
2. Masques jetés dans la nature : "Ils mettront au moins une dizaine d'années à se dégrader" prévoit un chercheur bordelais
   Sud Ouest, 24 Mai 2020
3. Dans la nature, en combien de temps un masque chirurgical se degrade-t-il ?
   Mon Quotidien, 5 Septembre 2020
4. Info ou Intox : Un masque pollue pendant 450 ans
   Le pharmacien de France, Septembre-Octobre 2020
5. Le grand format : dans les secrets de fabrication du chewing-gum
   la Journal Télévisé du 20h de *TF1*, 19 Octobre 2020
6. Emballages : les plastiques bio le sont-ils vraiment ?
   Journal Télévisé du 20h de *France 2*, 2 Novembre 2020
7. Du plastique dans les chewing-gums : faut-il s'en inquiéter ?
   Le Parisien, 24 Mars 2023
8. Plastiques : Au-delà des apparences !
   Draw Me un materiau, 6 Novembre 2023

Vulgarisations :

1. Dans le cadre de Pint of Science le 9 mai 2022 intitulé « Polymère biosourcé : la panacée ? »
2. Dans le cadre du cycle des conférence Grand Public de Bordeaux INP le 6 février 2023 sur la valorisation des déchets plastiques
3. Cap Sciences autour de rencontre Grand Public-Chercheur Bureau des Enquetes (environ 2 fois par an depuis 2021).
4. Conférence Grand Public durant NT23 intitulé « Le plastique, c'est fantastique ! Quel avenir pour le matériau miracle devenu menace existentielle ? » à Arcachon le 7 Juin 2023
5. Participation à l'émission EcoLantah autour de la pollution plastique. Production String Theory (Sortie Septmbre 2024)
6. Création courte vidéo YouTube autour des polymères avec comme objectifs d'en créer une/ou plus par an.
   a. Les plastiques : Une brève introduction aux matériaux polymères
   b. La transition vitreuse expliquée avec des Lego

Associations :

1. Membre du comité de direction de la *Fresque du Plastique*
2. Animateur *Fresque du Climat*
3. Animateur *Fresque du Sexisme*