Title

Amino acids as bio-organocatalysts in ring-opening copolymerization for eco-friendly synthesis of biobased oligomers from vegetable oils

Abstract

Herein, we present an innovative synthetic approach for producing a diverse set of biobased oligomers. This method begins with olive oil and employs a wide variety of commercially available amino acids (AAs) as bio-organocatalysts, in addition to tetrabutylammonium iodide (TBAI) as a cocatalyst, to synthesize various biobased oligomers. These biobased oligomers were strategically prepared starting from epoxidized olive oil (EOO) and a variety of cyclic anhydrides (phthalic, PA; maleic, MA; succinic, SA; and glutaric, GA). Among the amino acids tested as bio-organocatalysts, l-glutamic acid (l-Glu) showed the best performance for the synthesis of both poly(EOO-co-PA) and poly(EOO-co-MA), exhibiting 100% conversion at 80 °C in 2 hours, whereas the formation of poly(EOO-co-SA) and poly(EOO-co-GA) required more extreme reaction conditions (72 hours under toluene reflux conditions). Likewise, we have succeeded in obtaining the trans isomer exclusively for the MA based-oligomer within the same synthetic framework. The obtained oligomers were extensively characterized using techniques including NMR, FT-IR, GPC and TGA. A series of computational simulations based on density functional theory (DFT) and post-Hartree Fock (post-HF) methods were performed to corroborate our experimental findings and to obtain an understanding of the reaction mechanisms. © 2024 The Royal Society of Chemistry.

Authors

Werlinger F.; Beroíza-Duhart M.; Douglas-Gallardo O.A.; Oyarzo-Aro S.; Valenzuela

M.L.; Trofymchuk O.S.; Flores M.E.; Martínez J.

Author full names

Werlinger, Francisca (54404009600); Beroíza-Duhart, Monserrat (59074439800); Douglas-Gallardo, Oscar A. (56152263900); Oyarzo-Aro, Silvia (59076576500); Valenzuela, Maria Luisa (7102612018); Trofymchuk, Oleksandra S. (36020634000); Flores, Mario E. (36091131600); Martínez, Javier (55712374000)

Author(s) ID

54404009600; 59074439800; 56152263900; 59076576500; 7102612018; 36020634000; 36091131600; 55712374000

Year

2024

Source title

Organic and Biomolecular Chemistry

Volume

22.0

Issue

20

Page start

4135

Page end

4144

Page count

9.0

DOI

10.1039/d4ob00339j

Link

https://www.scopus.com/inward/record.uri?eid=2-s2.0-85192480392&doi=10.1039%2fd4ob00339j&partnerID=40&md5=535ada9175850775861db5040f957650

Affiliations

Facultad de Ciencias Químicas y Farmacéuticas, Departamento de Química

Orgánica y Fisicoquímica, Universidad de Chile, Santiago, 8380492, Chile; Instituto de Ciencias Químicas, Facultad de Ciencias, Isla Teja, Universidad Austral de Chile, Valdivia, 5090000, Chile; Universidad Autónoma de Chile, Facultad de Ingeniería, Instituto de Ciencias Aplicadas, Grupo de Investigación en Energía y Procesos Sustentables, Av. El Llano Subercaseaux, Santiago, 2801, Chile

Authors with affiliations

Werlinger F., Facultad de Ciencias Químicas y Farmacéuticas, Departamento de Química Orgánica y Fisicoquímica, Universidad de Chile, Santiago, 8380492, Chile, Instituto de Ciencias Químicas, Facultad de Ciencias, Isla Teja, Universidad Austral de Chile, Valdivia, 5090000, Chile; Beroíza-Duhart M., Instituto de Ciencias Químicas, Facultad de Ciencias, Isla Teja, Universidad Austral de Chile, Valdivia, 5090000, Chile; Douglas-Gallardo O.A., Instituto de Ciencias Químicas, Facultad de Ciencias, Isla Teja, Universidad Austral de Chile, Valdivia, 5090000, Chile; Oyarzo-Aro S., Instituto de Ciencias Químicas, Facultad de Ciencias, Isla Teja, Universidad Austral de Chile, Valdivia, 5090000, Chile; Valenzuela M.L., Universidad Autónoma de Chile, Facultad de Ingeniería, Instituto de Ciencias Aplicadas, Grupo de Investigación en Energía y Procesos Sustentables, Av. El Llano Subercaseaux, Santiago, 2801, Chile; Trofymchuk O.S., Facultad de Ciencias Químicas y Farmacéuticas, Departamento de Química Orgánica y Fisicoquímica, Universidad de Chile, Santiago, 8380492, Chile; Flores M.E., Instituto de Ciencias Químicas, Facultad de Ciencias, Isla Teja, Universidad Austral de Chile, Valdivia, 5090000, Chile; Martínez J., Instituto de Ciencias Químicas, Facultad de Ciencias, Isla Teja, Universidad Austral de Chile, Valdivia, 5090000, Chile

Index Keywords

Amino Acids; Catalysis; Green Chemistry Technology; Molecular Structure; Plant Oils; Polymerization; Polymers; Quaternary Ammonium Compounds; Amino acids; Computation theory; Density functional theory; Olive oil; Organocatalyst; amino acid; polymer; quaternary ammonium derivative; vegetable oil; Amino-acids; Bio-based; Co catalysts; Eco-friendly; L-glutamic acids; Organocatalysts; Performance; Phthalic; Ring opening copolymerization; Synthetic approach; catalysis; chemical structure; chemistry; green chemistry; polymerization; synthesis; Oligomers

Chemicals/CAS

amino acid, 65072-01-7

Funding Details

Fondo Nacional de Desarrollo Científico y Tecnológico, FONDECYT, (3220023, 1220241, 11230124, FOVI230027); Fondo Nacional de Desarrollo Científico y Tecnológico, FONDECYT

Funding Texts

F. W. is grateful for FONDECYT Postdoctoral fellowship 3220023. O. S. T. is grateful for FONDECYT Regular fellowship 1220241. J. M. is grateful for FONDECYT Iniciaci\u00F3n fellowship 11230124 and FOVI230027.

References

Kamphuis A.J., Picchioni F., Pescarmona P.P., Green Chem., 21, pp. 406-448, (2019); Anastas P., Eghbali N., Chem. Soc. Rev., 39, pp. 301-312, (2010); Akkouri N., Baba K., Ait Elkassia A., Int. J. Pavement Res. Technol., 16, pp. 760-779, (2023); Fernandez-Silva S.D., Delgado M.A., Ruiz-Mendez M.V., Giraldez I., Garcia-Morales M., Ind. Crops Prod., 185, (2022); Bhatia S.K., Gurav R., Choi T.-R., Kim H.J., Yang S.-Y., Song H.-S., Park J.Y., Park Y.-L., Han Y.-H., Choi Y.-K., Kim S.-H., Yoon J.-J., Yang Y.-H., Bioresour. Technol., 302, (2020); Hosseinzadeh-Bandbafha H., Li C., Chen X., Peng W., Aghbashlo M., Lam S.S., Tabatabaei M., J. Hazard. Mater., 424, (2022); Ahmed R.B., Hossain K., Constr. Build. Mater., 230, (2020); Orjuela A., Clark J., Curr. Opin. Green Sustainable Chem., 26, (2020); Lam C.-M., Yu I.K.M., Hsu S.-C., Tsang D.C.W., J. Cleaner Prod., 199, pp. 840-848, (2018); Rodriguez-Jorquera I.A., Siroski P., Espejo W., Nimptsch J., Choueri P.G., Choueri R.B., Moraga C.A., Mora M., Toor G.S., Integr. Environ. Assess. Manage., 13, pp. 360-370, (2017); Dharmalingam B., Balamurugan S., Wetwatana U., Tongnan V., Sekhar C., Paramasivam B., Cheenkachorn K., Tawai A., Sriariyanun M., Fuel, 340, (2023); Sathish T., Muthukumar K., Abdulwahab A., Rajasimman M., Saravanan R., Balasankar K., Fuel, 333, (2023); Wei H., Wang Q., Zhang R., Liu M., Zhang W., Process Biochem., 125, pp. 171-180, (2023); Maidin N.A., Rahman M.H.A., Ahmad M.N., Osman M.H., Wahid M.K., Ahmad U.H., Tan H.S., Anuar N.F.B.W.; Maotsela T., Danha G., Muzenda E., Procedia Manufacturing, 35, (2019); Werlinger F., Caprile R., Cardenas-Toledo V., Tarraff B., Mesias-Salazar A., Rojas R.S., Martinez J., Trofymchuk O.S., Flores M.E., ACS Omega, 8, pp. 21540-21548, (2023); Elkelawy M., Etaiw S.E.-D.H., Bastawissi H.A.-E., Marie H., Radwan A.M., Dawood M.M., Panchal H., J. Therm. Anal. Calorim., 147, pp. 6375-6391, (2022); Keijer T., Bakker V., Slootweg J.C., Nat. Chem., 11, pp. 190-195, (2019); Wang Z., Hellweg S., ACS Sustainable Chem. Eng., 9, pp. 6939-6951, (2021); Zuin V.G., Kummerer K., Nat. Rev. Mater., 7, pp. 76-78, (2022);

Kuranska M., Benes H., Polaczek K., Trhlikova O., Walterova Z., Prociak A., J. Cleaner Prod., 230, pp. 162-169, (2019); Mahadi M.B., Azmi I.S., Kadir M.Z.A., Mohamed N., Rahman M.A., Jalil M.J., Biomass Convers. Biorefin., pp. 1-9, (2023); Lim S.W., Kansedo J., Tan I.S., Tan Y.H., Nandong J., Lam M.K., Ongkudon C.M., Process Biochem., 130, pp. 715-733, (2023); Tian L., Li H., Song X., Ma L., Li Z.-J., J. Environ. Chem. Eng., 10, (2022); Chavan S., Yadav B., Tyagi R.D., Wong J.W.C., Drogui P., Bioresour. Technol., 369, (2023); Rodrigues J.D.O., Andrade C.K.Z., Quirino R.L., Sales M.J.A., Prog. Org. Coat., 162, (2022); Werlinger F., Caballero M.P., Trofymchuk O.S., Flores M.E., Moreno-Villoslada I., de la Cruz-Martinez F., Castro-Osma J.A., Tejeda J., Martinez J., Lara-Sanchez A., Util., 79, (2024); Polaczek K., Kuranska M., Prociak A., J. Cleaner Prod., 359, (2022); Martinez J., De La Cruz-Martinez F., De Sarasa Buchaca M.M., Caballero M.P., Ojeda-Amador R.M., Salvador M.D., Fregapane G., Tejeda J., Castro-Osma J.A., Lara-Sanchez A., J. Environ. Chem. Eng., 9, (2021); Khatoon H., Iqbal S., Irfan M., Darda A., Rawat N.K., Prog. Org. Coat., 154, (2021); Okabayashi R., Ohta Y., Yokozawa T., Polym. Chem., 10, pp. 4973-4979, (2019); Zhang X., Sun P., Jiang Y., Liao S., Chem. - Asian J., 18, (2022); Li M.-Q., Luo Z.-X., Yu X.-Y., Tian G.-Q., Wu G., Chen S.-C., Wang Y.-Z., Macromolecules, 56, pp. 2465-2475, (2023); Brandolese A., Della Monica F., Pericas M., Kleij A.W., Macromolecules, 55, pp. 2566-2573, (2022); Liao X., Su Y., Tang X., Sci. China: Chem., 65, pp. 2096-2121, (2022); Zhao Y., Zhu S., Liao C., Wang Y., Lam J.W.Y., Zhou X., Wang X., Xie X., Tang B.Z., Angew. Chem., Int. Ed., 60, pp. 16974-16979, (2021); Diment W.T., Lindeboom W., Fiorentini F., Deacy A.C., Williams C.K., Acc. Chem. Res., 55, pp. 1997-2010, (2022); Ma Y., You X., Zhang J., Wang X., Kou X., Liu S., Zhong R., Li Z., Angew. Chem., Int. Ed., 62, (2023); Xie R., Zhang Y.-Y., Yang G.-W., Zhu X.-F., Li B., Wu G.-P., Angew. Chem., Int. Ed., 60, pp. 19253-19261, (2021); Zhang J., Wang L., Liu S., Kang X., Li Z., Macromolecules, 54, pp. 763-772, (2021); Wang J., Zhu Y., Li M., Wang Y., Wang X., Tao Y., Angew. Chem., Int. Ed., 61, (2022); Fukushima K., Nozaki K., Macromolecules, 53, pp. 5018-5022, (2020); Claver C., Bin Yeamin M.,

Reguero M., Masdeu-Bulto A.M., Green Chem., 22, pp. 7665-7706, (2020); Roshan K.R., Jose T., Kim D., Cherian K.A., Park D.W., Catal. Sci. Technol., 4, pp. 963-970, (2014); Kadir M.Z.A., Motiyus A.S., Azmi I.S., Jalil M.J., Biomass Convers. Biorefin., pp. 1-9, (2023); Longo J.M., Sanford M.J., Coates G.W., Chem. Rev., 116, pp. 15167-15197, (2016); Hu L.-F., Zhang C.-J., Chen D.-J., Cao X.-H., Yang J.-L., Zhang X.-H., ACS Appl. Polym. Mater., 2, pp. 5817-5823, (2020); Babahan-Bircan I., Demirkaya I., Hasan S.O.H., Thomas J., Soucek M.D., Prog. Org. Coat., 165, (2022); Thomas J., Patil R., Ind. Eng. Chem. Res., 62, pp. 1725-1735, (2023); Vallin A., Ferretti F., Campaner P., Monticelli O., Pellis A., ACS Sustainable Chem. Eng., 11, pp. 9654-9661, (2023); Van Damme S., Bultinck P., Fias S., J. Chem. Theory Comput., 5, pp. 334-340, (2009); Marenich A.V., Cramer C.J., Truhlar D.G., J. Phys. Chem. B, 113, pp. 6378-6396, (2009); Grimme S., J. Chem. Phys., 118, pp. 9095-9102, (2003); Douglas-Gallardo O.A., Shepherd I., Bennie S.J., Ranaghan K.E., Mulholland A.J., Vohringer-Martinez E., J. Comput. Chem., 41, pp. 2151-2157, (2020); Neese F., Wiley Interdiscip. Rev.: Comput. Mol. Sci., 2, pp. 73-78, (2012); Neese F., Wiley Interdiscip. Rev.: Comput. Mol. Sci., 12, (2022); Caldeweyher E., Bannwarth C., Grimme S., J. Chem. Phys, 147, (2017); Tomasi J., Mennucci B., Cammi R., Chem. Rev., 105, pp. 2999-3094, (2005)

Correspondence Address

; ; J. Martínez; Instituto de Ciencias Químicas, Facultad de Ciencias, Isla Teja, Universidad Austral de Chile, Valdivia, 5090000, Chile; email: javier.martinez@uach.cl

Publisher

Royal Society of Chemistry

ISSN

14770520

CODEN

OBCRA

PubMed ID

38712466.0

Language of Original Document

English

Abbreviated Source Title

Org. Biomol. Chem.

Document Type

Article

Publication Stage

Final

Source

Scopus

EID

2-s2.0-85192480392