

From cationic organocatalysts to supramolecular chemistry, toward greener silicone materials

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Silicones or polyorganosiloxanes (R¹R²Si-O)_n are polymers with outstanding chemical and physical properties valorized in everyday life in a wide range of industrial applications: construction, automotive, electronics, medicine, personal care¹ etc. As a result, the growth forecasts for these materials are substantial with a compound annual growth rate (CAGR) of 7.4% from 2021 to 2030.² Nevertheless, harmonious economic development of silicones must also take up the challenge of the ecological transition by answering two important questions regarding i) the new regulatory requirements on materials purity, particularly in terms of cyclic content, and ii) the recycling of materials.

In this context, the results dealing with the valorization of ionic liquids as catalysts for the ring-opening polymerization of organocyclosiloxane will be presented. In particular, the use of a specific Brönsted acid ionic liquid (BAIL) has allowed the design of linear PDMS's of controlled molar masses up to 23 kg.mol⁻¹ and with an amount of cyclic byproducts lower than in a classical cationic process. Moreover, the kinetics were fast and end chain natures were efficiently controlled.³

The potential of the Aza-Michael reaction will also be reported. Indeed, this is a simple and accessible addition reaction performed at moderate temperature, possibly without a catalyst and without releasing by-products.⁴ Its versatility has allowed designing specific structures thanks to the availability of a multitude of Michael acceptors and Michael donors. ^{5,6,7}

Finally, various examples will be given for showing how ionic, zwitterionic modified silicones^{6,7} can bring supramolecular properties and therefore make reachable self-Healable, recyclable silicone materials...

References

1.T. Köhler, A. Gutacker, E. Mejía, Org. Chem. Front, 2020, 7, 4108-4120

2. https://www.globenewswire.com/en/news-release/2022/10/12/2532848/0/en/Global-Silicone-Market-Size-to-grow-USD-30-9-Billion-by-2030 [25 April 2023]

3. W. Nzahou Ottou, A. Boulègue Mondière, H. Parisot, D. Blanc, D. Portinha, E. Fleury, Polymer Chem, submitted

4. A. Genest, D. Portinha, E. Fleury, F. Ganachaud, Prog. Polym. Sci., 2017, 8, 61-110

5. A. Genest, S. Binauld, E. Pouget, F. Ganachaud, E. Fleury, D. Portinha, Polymer Chem., 2017, 3, 624-630

6. A. Genest, D. Portinha, E. Pouget, K. Lamnawar, F. Ganachaud, E. Fleury, Macromol. Rapid Commun. 2021, 42, 2000372

7. L. Fauvre, E. Fleury, F. Ganachaud, D. Portinha, ACS Appl. Polym. Mater. 2023, 5, 2, 1229–1240

8. E. Fleury, F. Ganachaud, D. Portinha, G. Duaux, A. Genest, E. Pouget. Silicones Materials, Elkem patent, WO 2019/166507