NITROXIDE-MEDIATED POLYMERIZATION OF BIO-BASED FARNESENE AND GLYCIDYL METHACRYLATE

Sharmaine B. Luk, McGill University, Department of Chemical Engineering, Montreal, Canada
sharmaine.luk@mail.mcgill.ca
Milan Marić, McGill University, Department of Chemical Engineering, Montreal, Canada

Key Words: bio-based, nitroxide-mediated polymerization, farnesene, methacrylate

There is increasing interest in using bio-based monomers to synthesize polymers that have comparable properties to petroleum-derived polymers. Terpenes like farnesene and myrcene have multiple unsaturated carbon-carbon bonds that can be polymerized like commonly known dienes (i.e. butadiene, isoprene). Farnesene is naturally found in essential oils and released as a pheromone to repel insects, but can also be produced through microbial pathways. In this work, farnesene (Far) and glycidyl methacrylate (GMA) were randomly copolymerized via nitroxide-mediated polymerization (NMP). Traditionally, NMP of methacrylates is not well-controlled due to slow recombination between the nitroxide radical and growing radical chain.[1-2] The succinamidyl ester form of the commercial BlocBuilder MA initiator, NHS-BlocBuilder, shows good control over NMP of methacrylates with the addition of 5-10 mol% of controlling monomer like styrene, without any additional free nitroxide.[3] At 120°C, copolymerizations of Far and GMA at various molar compositions without controlling monomer were done using NHS-BlocBuilder in bulk. Reactivity ratios of Far/GMA copolymerization were determined to be r_{Far} = 0.58 and r_{GMA} = 0.25 and the Mayo-Lewis plot is shown in Figure 1. For Far-rich compositions, dispersity was ~1.4 and showed linear chain growth. GMA-rich copolymerizations were also done at 90°C and showed good control suggesting that farnesene can act as a controlling monomer for NMP of GMA. Chain extension of Far/GMA random copolymers will be done with styrene to investigate chain-fidelity. Furthermore, a newly developed initiator based on a new class of alkoxyamines[4] will be used to copolymerize farnesene and GMA and its kinetics will be compared with NHS-BlocBuilder.

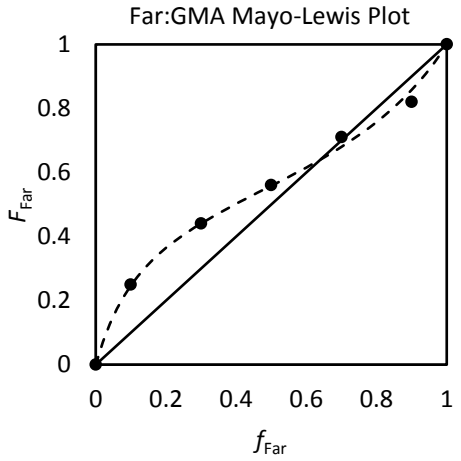

Figure 12: Mayo-Lewis plot of farnesene and GMA random copolymerization done at 120℃ in bulk with NHS-BlocBuilder. Cumulative copolymer composition is plotted as a function of initial monomer molar composition to determine relative reactivity ratios.

1. Guillaneuf, Y.; Gigmes, D.; Marque, S. R. A.; Tordo, P.; Bertin, D., *Macromol. Chem.Phys.* 2006, *207* (14), 1278-1288.
2. Nicolas, J.; Dire, C.; Mueller, L.; Belleney, J.; Charleux, B.; Marque, S. R. A.; Bertin, D.; Magnet, S.; Couvreur, L., *Macromolecules* 2006, *39* (24), 8274-8282.
3. Moayeri, A.; Lessard, B.; Maric, M., *Polym. Chem.* 2011, *2* (9), 2084-2092.
4. Ballard, N.; Aguirre, M.; Simula, A.; Agirre, A.; Leiza, J. R.; Asua, J. M.; van Es, S., *ACS Macro Lett.* 2016, *5* (9), 1019-1022.