

KINETIC PHENOMENA IN MECHANOCHEMICAL DEPOLYMERIZATION OF POLY(STYRENE)

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The accumulation of synthetic plastic waste on earth is an increasing global problem. The most abundantly manufactured and discarded plastics today are polyolefins.¹ Currently, most of polyolefin waste is landfilled, incinerated, or leaked into the environment. Mechanical recycling suffers from loss of performance properties and inflexibility in acceptable feedstock composition.² Chemical recycling via depolymerization, which converts waste polyolefins into useful chemical feedstocks, such as monomers and small molecules, is a promising solution to transition polymers to a circular economy. While polyolefin depolymerization through catalytic pyrolysis is heavily researched, the process is energy intensive and control over selectivity is challenging.³ Mechanochemistry offers a novel approach that allows for depolymerization of solid polymer feedstock at nominally ambient conditions, and thus has the potential to be a centerpiece in the chemical recycling solution to the global problem of plastic waste. Specifically, mechanochemistry uses mechanical forces in ball mills or similar device to provide energy and induce contacts between surfaces to drive chemical transformations.^{4,5}

Poly(olefin) depolymerization in a vibratory ball mill was studied using poly(styrene) (PS) as a model feedstock, building on a proof-of-concept report by Balema et al.⁶

Monomeric styrene was the primary depolymerization product alongside oxygenates like benzaldehyde as minor products. Increased monomer yields and the observation of the latter indicate that molecular oxygen plays a key role in PS activation and that oxygenates may be formed as intermediates. In a sealed reactor, the maximum styrene yield was reached after 160 min, while styrene was formed at a constant rate with continuous removal of monomers through an effluent gas stream (Figure 1). This shows that repolymerization of styrene becomes favored in the ball mill when a certain density is reached as it is in thermochemical reactions below the ceiling temperature of PS. Continuous removal of styrene allows for keeping its concentrations inside the ball mill sufficiently low and collecting the product in an environment where it can be stabilized. In addition, the monomer yield was enhanced when bimodal PS was milled with boric acid (BA). Inclusion of additional chemical additives allow for the illustration of particle-scale kinetic effects not present in homogeneous fluid-phase reactors, such as a decrease in monomer yield when the amount of BA was increased past an optimal ratio relative to PS, which can be rationalized as due to dilution of PS particles by additional BA particles, resulting in fewer occurrences of desirable monomer-generating bi-particle reaction events.

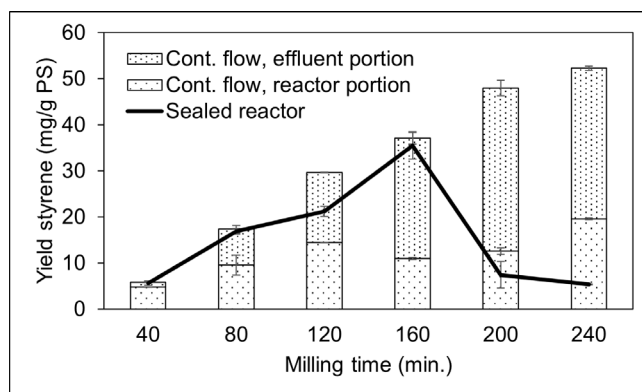


Figure 1: Styrene yield with milling time quantified by GC, continuous flow compared to sealed batch reactor.

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