

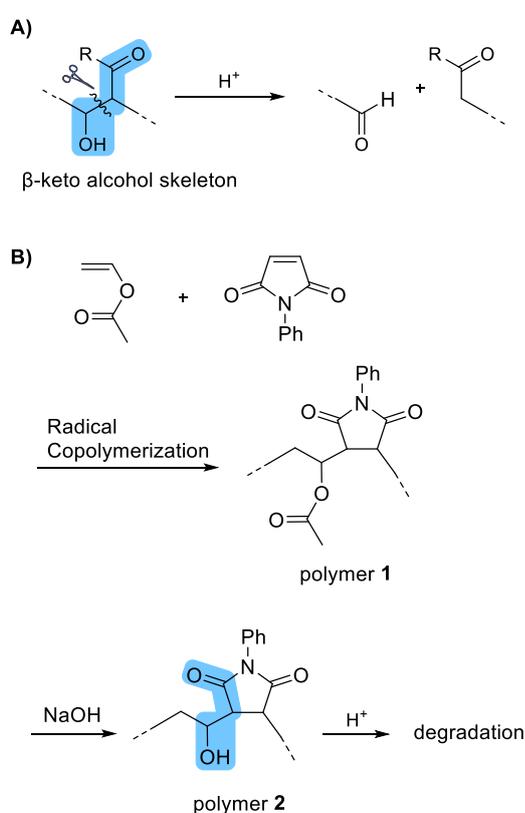
## Vinyl polymers degradable through main chain scission by retro-aldol reaction over the backbone and pendants

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Retro-aldol reaction (**Scheme A**), proceeding in a  $\beta$ -keto alcohol skeletons (highlighted by light blue), is known as a common tool for the cleavage of carbon-carbon bond in organic synthetic chemistry. We have envisioned that the reaction is also effective for the degradation of vinyl polymers through main chain scission.

In order to incorporate  $\beta$ -keto alcohol skeletons covering over polymer backbone and pendants, the radical copolymerization of an equimolar mixture of vinyl acetate (VAc) and *N*-phenyl maleimide (PMI), a pair of electron-rich and electron poor monomer for the alternative sequence, was conducted (**Scheme B**). The polymer **1** had a number-averaged molar mass ( $M_n$ ) and dispersity of molar mass ( $\mathcal{D}$ ) of 5200 and 1.76, respectively, and the composition was [VAc]/[PMI]=30/70. Thus, **1** was not an ideal alternating copolymer. The hydrolysis of **1** with NaOH was conducted; the degree of saponification of VAc units was 87%, while the  $M_n$  was decreased to 1900 ( $\mathcal{D} = 1.08$ ). The obtained **2** was then treated with 3 equiv. of hydrochloride in a cosolvent of water and dimethyl sulfoxide. The  $M_n$ s of the polymer were gradually decreased and reached 620 after 5 days, suggesting a possibility of the main chain scission by retro-aldol reaction. Additional experiments to confirm the reaction mechanism is in progress.



**Scheme A)** Retro-aldol reaction under acid condition. **B)** Copolymerization of vinyl acetate and *N*-phenyl maleimide.