

POST-POLYMERIZATION MODIFICATION VIA MASKED KETENES

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Nov. 21, 2013

INTRODUCTION:

Cross-linked polymers and polymers bearing various functional groups can be applied to important fields including drug-delivery, coating/adhesion, and microelectronics.^{1,2} While a variety of polymerization methods have been developed to synthesize polymers with controlled molecular weight, composition, and architecture, the synthesis of value-added polymers with high-level controls still presents a challenge in macromolecular science. Post-polymerization modification (PPM) is an attractive approach for the preparation of cross-linked and diversely functionalized polymers from a single precursor.² Several reactions for PPM have been investigated, including Cu^I-catalyzed azide-alkyne cycloaddition. However, the Cu catalyst forms complexes with the triazole ring, complicating purification and altering the polymer's properties.³ Among the reactions for PPM, ketene chemistry has been shown as a robust method. Masked ketene generates non-reactive byproducts upon catalyst-free thermolysis. And the resulting ketene group can be used as both a cross-linker and a functionalization agent (Figure 1), expanding the current PPM toolbox.⁴

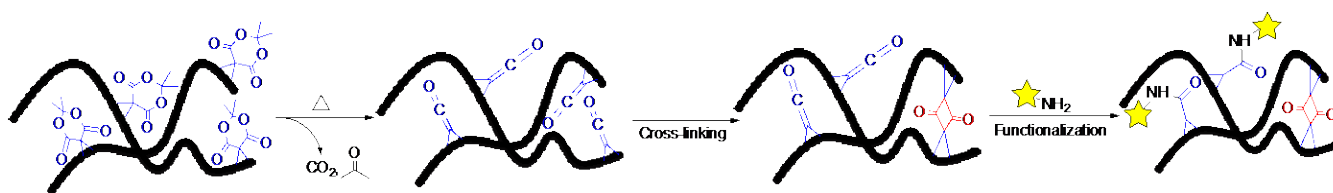


Figure 1. Meldrum's acid thermolysis forms a ketene, acetone and CO₂. The ketene can either dimerize to the cyclobutanedione, or act as an electrophile to afford the corresponding amide (or ester). Adapted from Ref. 3.

MELDRUM'S ACID AS A KETENE PRECURSOR IN POLYMER CHEMISTRY

Since the discovery by Hermann Staudinger in 1905,⁵ ketene has been used extensively in the synthesis of many small molecules including β -lactam ring systems.⁶ However, there was no reliable and user-friendly method to access ketenes in materials, because ketenes tend to dimerize or undergo nucleophilic reactions to form undesired products leading to changes in the reaction stoichiometry and altering the final molecular weight of the product. Thus, the use of ketene was neglected until its derivatives were used in living anionic polymerization by Sudo and Endo in 1999.⁷ With the discovery of Meldrum's acid (MA) as a ketene precursor, Hawker *et al.* recently incorporated MA to a number of polymers.⁴ Thermal treatment of MA resulted in the loss of acetone and carbon dioxide, thereby yielding polymers bearing ketenes. Model studies showed that heating dibenzyl MA to 200 °C or higher results in efficient formation of ketenes, which in the absence of a nucleophile undergoes dimerization to form

diketones.⁸ Monomers containing MA were synthesized for both radical and ring-opening metathesis polymerizations.⁴ The utility of thermolyzed MA for PPM was demonstrated by patterning an amine-functionalized fluorescent dye to the surface of a polymer containing MA using microcontact printing. The thermally generated ketenes cross-link the polymer thin films while simultaneously react with nucleophiles providing a reactive surface for the attachment of a variety of substrates. The efficiency of cross-linking by MA-based polymer was also illustrated by synthesis of cross-linked polyethylene.⁹

LOWERING TEMPERATURE FOR KETENE FORMATION

Although the thermolysis of MA is a useful way to generate ketenes in polymeric structures, the high temperature required for ketene formation reduces its applicability. Thus, there is a need to significantly lower the temperature of thermolysis. Two strategies, Lewis base activation and Brønsted acid activation, were investigated to achieve this goal (Figure 2).¹⁰ Further studies use molecular design and synthesis, crystal structure analysis, and computational studies of transition state structure to provide information on the molecular interactions governing MA reactivity.¹⁰

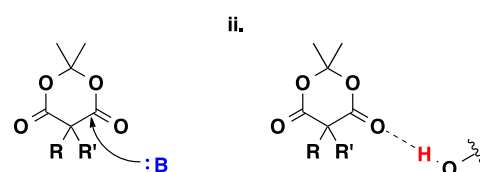


Figure 2. Pathways to lower the thermolysis temperature of Meldrum's acid derivatives. Adapted from Ref. 10.

SUMMARY

Meldrum's acid as a ketene precursor was successfully incorporated into polymers, expanding the PPM toolbox. Using this precursor with tunable thermo-stability, ketene's unique and versatile chemistry enables a variety of functions and subsequent applications in material science. The success of masked ketene in polymer chemistry also inspires ongoing research on incorporating other masked highly reactive groups into macromolecules.

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