

共役置換反応による不飽和ポリエステルは無溶媒分解：主鎖構造・物性が分解性に与える効果

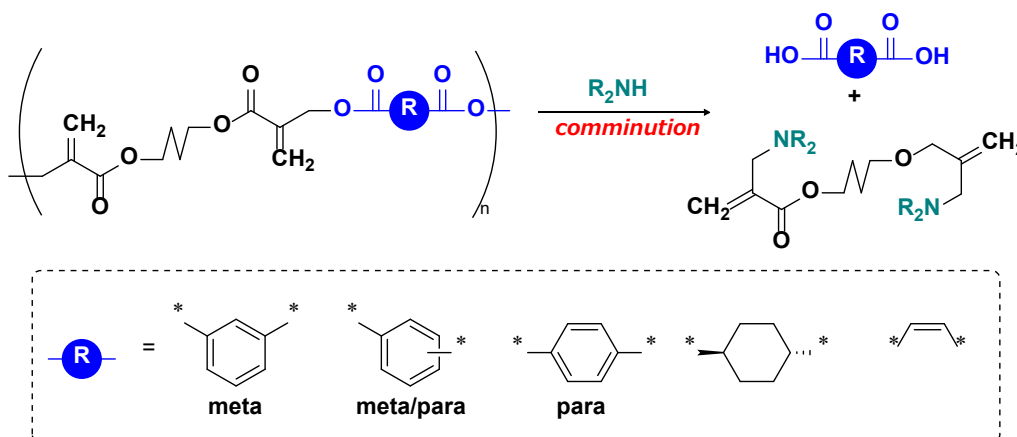
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Solvent-free degradation of unsaturated polyesters using conjugate substitution reaction: Effects of backbone structures and physical properties on degradability (<sup>1</sup>*Fac. Of Textile Sci. and Tech., Shinshu University*; <sup>2</sup>*RISM, Shinshu University*) Rikuto Kimura,<sup>1</sup> Yasuhiro Kohsaka<sup>1,2</sup>

Methacrylates bearing a leaving group at the allylic position accept nucleophilic conjugate substitution reactions under ambient condition. We recently applied this reaction to the main chain scission of unsaturated polyesters in organic solutions<sup>1</sup> and in a suspension with aqueous ammonia<sup>2</sup>. The previous work suggested similar degradation in solvent-free system. Herein, in order to investigate the relationship between polymer structure and degradability, a series of unsaturated polyesters **P1/2** with different dicarboxylic acids were examined. An equimolar secondary amine to the methacrylate skeletons in **P1/2** were added, and the mixture was comminuted in a mixer mill. The changes of molecular weights and conversions of methacrylate skeletons suggested that the main factor of degradability was not the leaving property, *i.e.* the acidity of dicarboxylic acids but the crystallinity of the polymers.

**Keywords** : unsaturated polyester; degradable polymer; main-chain scission; mechanochemistry

アリル位に脱離基を有するメタクリル酸エステルは、室温・大気下で求核剤と定量的に共役置換反応を起こす。著者らは最近、この反応を利用して、有機溶媒中<sup>1</sup>ならびにアンモニア水懸濁系<sup>2</sup>で分解可能な不飽和ポリエステルを報告した。先の研究で、同様の反応が無溶媒でも進行することを見出していたが、どのようなポリマーが分解しやすいかは不明であった。そこで、脱離成分となるジカルボン酸を変更した種々の不飽和ポリエステル **P1/2** を合成し、メタクリル骨格に対して等モル量の2級アミンとともにミキサールで粉碎・混合し、分子量減少や共役置換の進行度を追跡した。その結果、分解性はジカルボン酸の脱離能力(=酸性度)ではなく、主に結晶性に依存していることがわかった。



- 1) Y. Kohsaka, T. Miyazaki, K. Hagiwara, *Polym. Chem.* **2018**, 9, 1610. 2) Y. Kohsaka, K. Nagai, *Eur. Polym. J.* **2020**, 141, 110049.