

## ACETYLACETONATES MEDIATED ROP OF MODEL BIS-MPA-BASED CARBONATES

Michał Kawalec<sup>\*</sup>, Małgorzata Pastusiak, Joanna Jaworska,  
Piotr Kurcok, Piotr Dobrzyński

Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34 M. Skłodowskiej-Curie St., 41-819 Zabrze, Poland;  
<sup>\*</sup>michal.kawalec@cmpw-pan.edu.pl)

### ABSTRACT

Functional synthetic polymers have received considerable scientific interest and attention in recent years for their potential as promising novel materials enhancing properties of well-known polymers. Recently, attention has been directed towards aliphatic polycarbonates for the manufacture of temporarily used materials thanks to their biodegradability and biocompatibility<sup>1</sup>. In combination with their ready hydrolysis and low toxicity, aliphatic polycarbonates are attractive materials in (bio)medical and pharmaceutical field as gene carriers, drug delivery systems based on either nanoparticles, microspheres or hydrogels. Although the choice of commercially available monomers is relatively limited, several routes have been developed to prepare functional cyclic carbonates. At the moment scientific literature describes more than 80 functional cyclic carbonates with different pendant functions designed to improve properties of polymeric materials. Of the most versatile precursors are glycerol, pentaerythritol and 2,2-bis(hydroxymethyl)propionic acid (bis-MPA)<sup>2</sup>.

Herein, results of ring-opening polymerization of 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (MTC-Et) and benzyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (MTC-Bz) - functional model aliphatic carbonates mediated with coordination catalysts (acetylacetonates hydrates of zinc (II) ( $\text{Zn}(\text{acac})_2 \times \text{H}_2\text{O}$ ), lanthanum (III) ( $\text{La}(\text{acac})_3 \times \text{H}_2\text{O}$ ) and yttrium (III) ( $\text{Y}(\text{acac})_3 \times \text{H}_2\text{O}$ ) as well as scandium (III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate) hydrate) are presented. The polymerization experiments were carried out in bulk at temperature from 80°C to 150°C.

Acetylacetonate hydrates of zinc (II), lanthanum (III) and yttrium (III) were found to be efficient initiators of ring-opening polymerization of model functional cyclic carbonates carried out in bulk. Number-average molar masses of the obtained polycarbonates were relatively low but high-molar-mass fractions reached molar mass higher than 1'000'000 g/mol which is unusual in case of aliphatic carbonates ROP. Relatively broad molar mass distributions of polymers were observed in majority of products the most probably as a consequence of the carbonate pendant ester group transesterification. Noteworthy, bulkier substituent (benzyl) in vicinity of the ester group did not retard the secondary reactions. It was also noticed that even in case of one initiator relationship temperature-molar mass of products is relatively complex phenomenon.

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### References:

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<sup>2</sup>Tempelaar S., Mespouille L., Coulembier O., Dubois P., Dove A. P. *Chem. Soc. Rev.* **2013**, 42, 1312.