



Free radical polymerization study of glycerin carbonate methacrylate for the synthesis of cyclic carbonate functionalized polymers

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ABSTRACT

This article describes for the first time a complete study of the free radical polymerization (FRP) of (2-oxo-1,3-dioxolan-4-yl) methyl methacrylate or glycerin carbonate methacrylate (**GCMA**). This methacrylic cyclic carbonate compound allows the synthesis of polymers bearing cyclic carbonate functional groups which can be used for crosslinking reactions in other to form urethane linkages without the use of harmful isocyanates. Transfer reactions to the cyclic carbonate moiety were identified during the polymerization of **GCMA**. Moreover, a transfer constant of 0.011 was obtained when a cyclic carbonate compound, the acetate of glycerin carbonate is used as transfer agent during the polymerization of MMA. A calculation of the k_p^2/k_t value of **GCMA** in DMSO proves the high reactivity of this monomer since the value obtained ($245 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$) is almost 2 times higher than methyl methacrylate (MMA) value ($149 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$) in the same conditions. Glass transition temperatures of homopolymers of **GCMA** (114 and 134 °C) were measured for the first time. Finally the calculation of the reactivity ratios r_{MMA} (0.5) and r_{GCMA} (2.0) during the copolymerization of **GCMA** with MMA in DMSO, by the Macret's method shows again the high reactivity of this monomer.

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1. Introduction

Improvement in the thermal, mechanical, surface or physicochemical properties of polymers is an important challenge in polymer chemistry. In the current economic and environmental context, modification and improvement of already known polymers are preferred rather than the synthesis of polymers from new monomers. Cross-linking is thus the main method to improve properties starting from known and low molecular mass polymers [1]. Indeed it is a method of choice not only in order to improve the properties of the polymers but also to reach high molar masses starting from oligomers or prepolymers or also in

order to increase the glass transition temperature of materials. Cross-linking systems are extensively used for coatings since they allow a two-step synthesis, appreciated in industry: first the formulation and then the cross-linking on the substrate. Due to their cross-linking ability, polymers bearing reactive functionalities and curing agents have large potential for coatings and other related applications. Indeed, systems such as phenol-formol [2] or epoxy-amine [3] are widely used to cross-link polyacrylates. However the toxicity of compounds such as formaldehyde or glycidyl methacrylate, which is used as epoxy cross-linker, raises problems and all these compounds are increasingly controlled by the current regulations and should be replaced. Polyacrylates are also extensively used in urethane systems [4]. 2-Hydroxyethyl acrylate is a monomer of choice for the introduction of hydroxyl reactive

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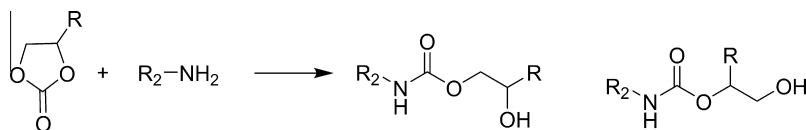


Fig. 1. Aminolysis reaction of cyclic carbonate with amine.

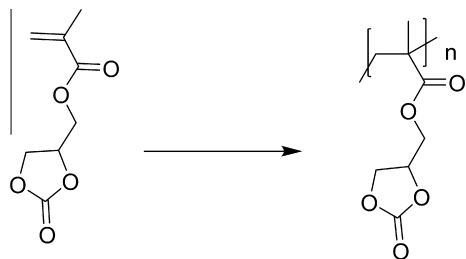


Fig. 2. Polymerization of (2-oxo-1,3-dioxolan-4-yl)methyl methacrylate (GCMA).

functionalities in polyacrylates. The cross-linking is carried out by adding a diisocyanate in formulation, reacting on hydroxyl functions and leading to carbamate linkages, responsible for the good properties of such kinds of coatings. The main drawback of this chemistry is also the use of isocyanates which are very harmful reactants. In order to overcome this issue, the synthesis of non-isocyanate polyurethanes has recently gained a great interest in chemical industry: step growth polymerization of dicyclo-carbonates and diamines can be an alternative route for the synthesis of conventional polyurethanes (Pus) without the use of isocyanates [5–12].

Interestingly, cyclic carbonates present in a polymer chain as pendant functional groups, could react with amines conducting in the formation of hydroxyl-urethane linkages with primary and secondary hydroxyl units (Fig. 1).

This kind of system can be used as a cross-linking system to obtain urethane linkages without the use of toxic isocyanates. Moreover, the presence of hydroxyl functions leads to supplementary hydrogen bonds which give advantages to polyhydroxyurethanes (PHUs) over conventional polyurethanes, with for example a lower porosity [13]. PHUs also exhibit higher chemical stability, since no thermally unstable biuret and allophanate units are formed, which usually go along with the reactions between diisocyanate and diols. Taking into account of this approach, homopolymers and copolymers bearing cyclic carbonate functional groups have been reported by various researchers [14–33].

The introduction of cyclic carbonate moieties by polymerization of cyclic carbonate monomers is an interesting possibility to obtain a functionalized polymer. Thus, scientists are paying increasing interest to monomers bearing reactive cyclic carbonate groups. We previously reported the synthesis and the applications of unsaturated cyclic carbonate compounds [34] which have two different reactive groups: the first one intended to polymerize or to copolymerize with other comonomers and the second

one for crosslinking reactions. (2-Oxo-1,3-dioxolan-4-yl)methyl methacrylate or glycerine carbonate methacrylate (GCMA) (Fig. 2) is the most studied monomer for the synthesis of carbonate functionalized polymers.

This monomer is currently commercialized by few companies such as Specific Polymers [35]. In the literature, several synthetic routes based on the synthesis of the carbonate moiety and the grafting of the methacrylic functionality were reported [17,26,36–48]. Among all these routes, the most interesting ones to obtain GCMA remain the carbonation of glycidyl methacrylate (Fig. 3, route (a)) and the transesterification of alkyl methacrylate such as methyl methacrylate with glycerin carbonate (Fig. 3, route (b)). Indeed carbonation is the most quantitative way to obtain pure cyclic carbonate and concerning the transesterification route, the use of methyl methacrylate which is cheap and easily available commercially and the use of glycerin carbonate which is partially biosourced are advantages.

Although some researchers studied the radical polymerization of GCMA [38,49,50]; according to its high reactivity, its polymerization was never entirely described. In order to allow the synthesis of polymer bearing carbonate moieties, particularly at the industrial scale, it is crucial to perform the complete study of the free radical polymerization of GCMA. So, herein we studied and compared the two most interesting methods (a and b) for the synthesis of GCMA, we studied the polymerization and the copolymerization of this monomer, and we also focused on the kinetics of polymerization. First, commercially available GCMA obtained both by carbonation and transesterification was copolymerized with some usual acrylic, methacrylic and styrenic monomers in order to study the influence of the synthesis method on radical polymerization. Then GCMA was homopolymerized by conventional radical polymerization in DMSO and compared to the carbonated homopolymer polyGMA. The high reactivity of GCMA was proven by the calculation of the characteristic constant of polymerizability ((k_p^2/k_t) where k_p is the propagation constant and k_t is the termination constant). And finally, the determination of reactivity ratios of GCMA and methyl methacrylate (MMA) during their copolymerization was also carried out. To the best of our knowledge, this is the first comprehensive study on copolymerization of GCMA by free radical polymerization.

2. Experimental

2.1. Materials and methods

The two samples of glycerin carbonate methacrylate synthesized by carbonation and by transesterification

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