Crosslinked Polymers Based on Monomers Derived from Renewable Resources and Their Application Potential

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Perspective

Crosslinked Polymers Based on Monomers Derived from Renewable Resources and Their Application Potential

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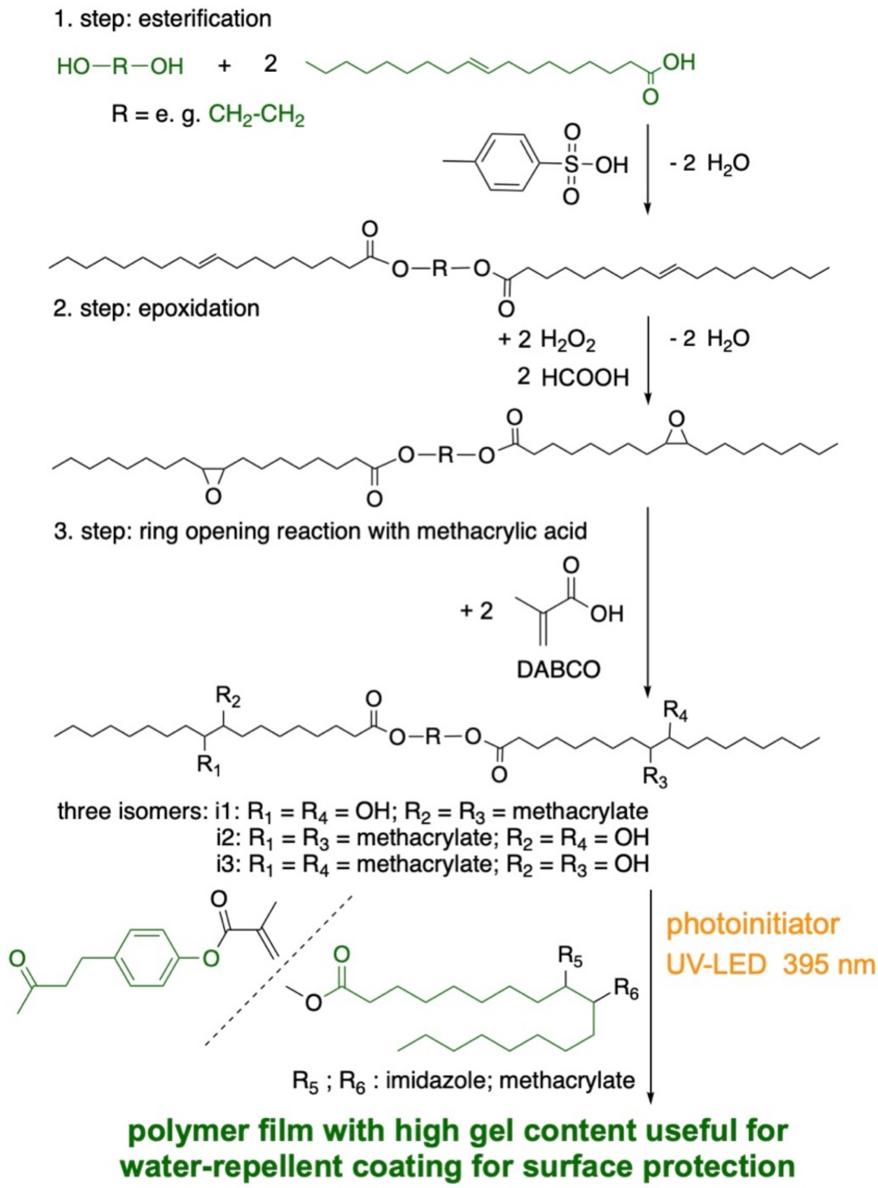
KEYWORDS

bio-based monomer, dimethacrylate, photo-initiated polymerization, crosslinked polymer, application potential

INTRODUCTION

Nowadays, there is no doubt that the modern society demands to search for alternative materials having the capability to replace fossil resources partially or completely in the future. Generation of fossil resources has needed a long period in the earth's history. Nevertheless, they have been used with continuous increasing amount in the last two centuries to generate materials. Thus, this topic closely relates to the chemical industry that has used fossil resources as both starting material for product manufacturing and energy source, which appears as very important for the usually highly energy intensive chemical processes. Two ways appear purposeful to solve this problem. These ways include both renewable energy sources and renewable materials. Sunlight seems useful as direct or indirect renewable energy source. Various plants produce a broad variability of biomass catalyzed by enzymes in the presence of sunlight as well. Discussions have continued in the literature to search regarding selection of available plant species outside the competition with food production for humans and animals, efficiency of product manufacturing from biomass, and re-using the material after its application.[1-4] Beside the high molecular weight natural products, such as cellulose, hemicellulose and lignin, low molecular weight compounds have received increased interest recently.[4-6] The latter include terpenes and triglycerides, as well as products derived from triglycerides like glycerin and various fatty acids. Nevertheless, some of them interfere the food chain, which appears critical in countries with high population density or regions with food shortage. Thus, resources based on waste have moved into the focus.

Furthermore, several bio-based linear aliphatic, aromatic, and cycloaliphatic compounds have been successfully converted into (meth)acrylates that are interesting monomers for manufacturing of polymers.[7-14] Among these bio-based monomers is a new dimethacrylate synthesized in three steps as shown in Scheme 1. The synthesis starts with esterification of oleic acid with ethylene glycol, it continues with epoxidation of the two double bonds of the ethylene dioleate, and ring opening reaction of the resulting diepoxy compound with methacrylic acid is the final step.[12] Moreover, the new bio-based dimethacrylate was polymerized in thin film using photoinitiated radical polymerization mechanism applying ultraviolet-technology (Scheme 1) to form an insoluble crosslinked polymer film showing high hydrophobicity detected by contact angle measurements.[12]Crosslinking polymerization of the bio-based dimethacrylate alone or in the presence of further bio-based methacrylates comprising aromatic structures resulted in glass transition temperature increase of the highly hydrophobic crosslinked polymer films that makes them interesting for application e. g. as water-repellent coating for surface protection. The latter may be of importance for surface protection against corrosion. Such materials possess additionally potential in medical application as long as the natural origin would not cause incompatible responses of the body that synthetic materials sometimes do.



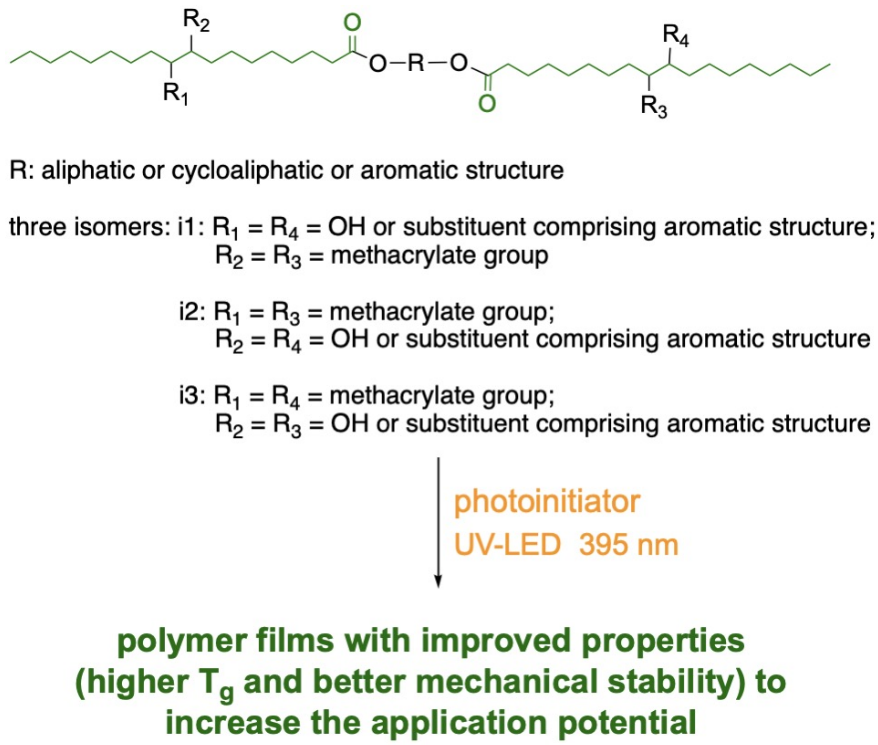
Scheme 1. Synthetic way to a bio-based dimethacrylate starting by esterification of oleic acid with a diol (e. g. ethylene glycol) catalyzed by *p* -toluene sulfonic acid (1. step), epoxidation of the double bonds of the diester with hydrogen peroxide in the presence of formic acid (2. step), and epoxy ring opening reaction with methacrylic acid catalyzed by 1,4-diazabicyclo[2.2.2]octane (DABCO, 3. step) resulting in three isomers (i1, i2, and i3) of the bio-based dimethacrylate. Photoinitiated radical polymerization of the dimethacrylate alone or in the presence of bio-based methacrylates comprising aromatic structures resulted in crosslinked polymer films showing water-repellent properties as detected by contact angle measurements.[12]

SOURCES FOR THE STARTING MATERIAL

Plant oil and fat represent main resources for triglycerides that are hydrolyzed into fatty acids and glycerol by chemical or enzymatic processes.[4,15] Though industrial use of plant oil and fat e. g. for biodiesel production from triglycerides as alternative to petrochemical diesel or for monomer synthesis compete with food production, only cooking oil available as waste from industry, restaurants or household should be utilized for fatty acid manufacturing. Furthermore, the glycerol formed as by-product in the biodiesel production may be useful for esterification of oleic acid instead of using ethylene glycol as shown in Scheme 1.[12] Ethylene glycol is obtained in two different ways; that is a petrochemical and a bio-based way. The latter is described as hydrolytic hydrogenolysis reaction of cellulose.[16,17] Lignin available in bark, wood and plants provides compounds comprising aromatic moieties derived from natural resources.[18,19]

STRUCTURAL VARIABILITY OF THE CROSSLINKABLE BIO-BASED MONOMER

Various structural modifications of the bio-based dimethacrylate may be possible by choosing different diol compounds for esterification with oleic acid resulting in variation of the bridge between the oleate structures on the one hand and by selection of different reagents for ring opening reaction of the epoxidized di-oleates that give a structural variation of the substituents R_1, R_2, R_3, and R_4 on the other hand (Scheme 1). The latter may contain either an OH-group or aromatic structure and two (meth)acrylate groups. As a result, the structure depicted in Scheme 2 represents only some possible structural modifications of the dimethacrylate derived from oleic acid and ethylene glycol, which was firstly described in 2021.[12]



Scheme 2. Possible structural modification of the dimethacrylate derived from oleic acid and ethylene glycol (Scheme 1) includes variation of both the linking moiety R and the substituents R_1, R_2, R_3, as well as R_4resulting in numerous possible bio-based dimethacrylates that may differ in the properties of both monomers and polymers made of them e. g. by photoinitiated polymerization. The efficiency of both processes, monomer manufacturing and polymer formation as well as the properties of the crosslinked polymer materials obtained are important for selection of the new materials for application.

APPLICATION POTENTIAL

Aspects for introduction of new starting materials in existing production processes for manufacturing of new products include availability and current economic affordability of the new raw material, efficiency of the manufacturing processes for both the product, e. g. monomer and further material derived of the product, e. g. crosslinked material. Furthermore, the manufacturing processes should agree with the principles of green chemistry.[20] Quantification of the efficiency of manufacturing processes includes for example the energy balance, atom economy, yield, reaction mass efficiency, process mass intensity, and environmental factor.[21-26]Moreover, the new products should address to gaps existing on the market or may be replacements showing improved properties relative to existing products. Though fossil resources are limited, partial or complete substitution of the fossil resources will be necessary sooner or later. Therefore, the new bio-based dimethacrylate described in the reference[12] is going to contribute to this topic. The new journal *Applied Research* was selected for publication of the scientific results obtained regarding the new bio-based dimethacrylate manufacturing and photocrosslinking resulting in hydrophobic crosslinked films to draw attention particularly for the use in practice. Here, the new highly hydrophobic material received from the dimethacrylate alone or in the presence of a bio-based methacrylate comonomer comprising an aromatic structure possesses huge potential. The two long alkyl substituents, which are available in each segment of the crosslinked polymer, contribute to the high hydrophobicity of the material derived from the bio-based dimethacrylate. Furthermore, the high hydrophobicity of the material makes it attractive for applications in corrosion protection e. g. of metal surfaces. At the present time, fluorinated polymers are commonly used to increase the hydrophobicity of surfaces although their manufacture has a negative impact on the environment.[27] Nowadays, substitution of fluorine comprising materials has received increased priority to solve this environmental issue. Here, the new bio-based dimethacrylate (Scheme 1) and a modified structure of the bio-based dimethacrylate e. g. as shown in Scheme 2, respectively, may become interesting alternatives to the currently used fluorinated polymers. 3D Printing can be seen as an additional application field where these monomers could receive additional attraction.[28-32] Particular manufacture of prothesis for medical uses or dental restauration addresses interesting challenges.[31,32]

The journal *Applied Research* together with its broad interested readership has accelerated scientific research in diverse fields, which strongly relate to application aspects. This covers applied research in industry for improving existing products and production processes as well as for the development of new products whose production proceeds in existing manufacturing plants. These facts may contribute to accelerate the transfer of recently obtained scientific results and newly developed products to manufacturing processes and making it feasible to bring new products to the market. Furthermore, the application aspects of the papers published in the journal *Applied Research* are going to widen the visual field of researchers working at institutes and universities. Moreover, this may encourage these researchers to include application aspects in their own work as well. The idea of applied research is deep-seated in research institutes such as Fraunhofer Institutes and Universities of Applied Sciences in Germany. The journal*Applied Research* may become the favorite journal for publication of scientific results focusing on application aspects derived from fundamental research. In addition, this journal represents a valuable source to provide recent research results with applied aspects for teaching in master and doctoral courses focusing on sustainable and green aspects.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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Veronika Strehmel accepted her professorship for Organic Chemistry focusing on Macromolecular Chemistry at the Niederrhein University of Applied Sciences in 2010. Beside *Polymer Chemistry* and*Polymerization Technology* , she has taught *Green Organic and Polymer Chemistry* . Furthermore, she has been private lecturer for Polymer Chemistry at the University of Potsdam since 2007, where she has taught *Photopolymerization* . As a member of the Institute for Coatings and Surface Chemistry of the Niederrhein University of Applied Sciences, her research has focused on ionic liquids as well as on monomers and polymers based on renewable resources. Prior to this, after completing her PhD at the Technical University of Merseburg, she pursued both applied research (Leuna Company; Fraunhofer Institute for Applied Polymer Research) and fundamental research (Stanford University; Martin-Luther University Halle-Wittenberg, where she received her habilitation in Polymer Chemistry in 2000; Institute for Thin Film Technology and Microsensorics; University of Potsdam).

Picture: Veronika Strehmel

Bernd Strehmel accepted his professorship for Coatings and New Materials at the Niederrhein University of Applied Sciences in 2011. Since 2017, he has chaired the Institute for Coatings and Surface Chemistry at the same institution in Krefeld. In the master module *Green Chemistry* , he has taught *Technical Photochemistry* since 2017. Prior to this, after completing his PhD at the Technical University of Merseburg, he pursued research at several national (TU Berlin, Humboldt-University of Berlin, University of Potsdam) and international universities (Stanford University, Bowling Green State University-Center for Photochemical Sciences) before he moved to Kodak after completion his habilitation at the Humboldt-University of Berlin.

There, he worked in R&D for the development of Computer to Plate materials for the graphic industry. He additionally has been a member of the reviewer board of the German Research Council (DFG) in the field 406: Material Science (Synthesis and Properties of Functional Materials) from 2016. In the German Chemical Society (GDCh), he was a member of the board of the Photochemistry division, which he chaired from 2018 to 2021.

Picture: Bernd Strehmel