

# Water-borne poly(meth)acrylates obtained from functional and renewable monomers

Citation for published version (APA):

Stouten, J. (2023). *Water-borne poly(meth)acrylates obtained from functional and renewable monomers*. [Doctoral Thesis, Maastricht University]. Maastricht University. <https://doi.org/10.26481/dis.20230620js>

## Document status and date:

Published: 01/01/2023

## DOI:

[10.26481/dis.20230620js](https://doi.org/10.26481/dis.20230620js)

## Document Version:

Publisher's PDF, also known as Version of record

## Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

## General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

[www.umlib.nl/taverne-license](http://www.umlib.nl/taverne-license)

## Take down policy

If you believe that this document breaches copyright please contact us at:

[repository@maastrichtuniversity.nl](mailto:repository@maastrichtuniversity.nl)

providing details and we will investigate your claim.

The main goal of this thesis was to investigate novel and functional biobased monomers in order to develop acrylic latexes based on biobased monomers for cross-linked film and coating applications. Two main modes of cross-linking were investigated, each requiring the incorporation of a functional side group in the polymer backbone. The first monomer was 4-oxocyclopentenyl acrylate (4CPA), which is able to dimerize under UV light. The second monomer is 2-(methacryloyloxy)ethyl vanillin (MEV), which can undergo imine formation in the presence of an amino functional cross-linker. The aim of the cross-linking step was firstly to improve the physical properties of the resulting film, but also to introduce value-added properties in the resulting applications, supporting the concepts of circularity and reducing environmental pollution.

The first part of this work focused on the exploration of the Reversible Addition-Fragmentation chain-Transfer (RAFT) controlled solution homo- and copolymerization of 4CPA (**Chapter 2**). In the homopolymerization of 4CPA, only low molecular weight polymers were obtained without cross-linking. Model studies showed that cross-linking likely occurs due to the participation of the cyclopentenone group in the RAFT controlled radical polymerization. Nonetheless, the selectivity between the acrylate and cyclopentenone group during RAFT polymerization was high enough to yield polymers containing intact cyclopentenone side groups according to  $^1\text{H}$  NMR spectroscopy. In the copolymerization of 4CPA with comonomers such as methyl acrylate (MA), isobornyl acrylate (IBOA), and lauryl acrylate (LA), higher monomer conversions and molecular weights were reached. In this case, copolymerization is a straightforward strategy to tune the thermal properties of the polymer, and reduce the degree of functionality along the polymer backbone. The cyclopentenone side groups belonging to the 4CPA were successfully dimerized under UV light to yield cross-linked freestanding films. The results were supported by a [2 + 2] photocyclodimerization reaction of the model molecule, 4-oxocyclopentenyl acetate, yielding the head-to-head and head-to-tail dimers. The cross-linked films showed a high gel fraction and increase in the glass transition temperature ( $T_g$ ) as a result of the UV irradiation.

The development of copolymers based on 4CPA and LA in chapter 2 was exploited in the synthesis of amphiphilic block copolymers in **Chapter 3**. The block copolymers consisting of poly(oligo(ethylene glycol) methyl ether acrylate) (POEGA) as the water-soluble block and a copolymer of 4CPA and LA as the hydrophobic block self-assembled after introduction in water. The micelles could serve as nano-sized drug vehicles. A series of nine block copolymers was synthesized consisting of different hydrophilic and hydrophobic block lengths. The 4CPA block copolymers could self-assemble in water either after direct dissolution, or by a solvent exchange method resulting in different morphologies and sizes. The micellar cores could be cross-linked after irradiation of UV light resulting in core-cross-linked micelles. The therapeutic drug doxorubicin (DOX) was successfully loaded in the micelles and cell viability essays indicated a high cytotoxicity towards breast adenocarcinoma cells as a result of the DOX loading. On the other hand, non-loaded micelles were not toxic to healthy cells at the evaluated concentrations in the cancer cell essay. Furthermore, 4CPA could serve as a UV cross-linkable monomer for the production of core-cross-linked drug delivery vehicles.

4CPA latexes were developed in **Chapter 4**. A RAFT controlled Polymerization Induced Self-Assembly (PISA) process was developed for the production of 4CPA latexes containing several biobased monomers. The investigated comonomers were butyl acrylate (BA), tetrahydrofurfuryl acrylate (THFA), IBOA, and 2-octyl acrylate (2OA). Using a POEGA macro-RAFT agent in a low temperature polymerization of 50 °C, stable and high solid content latexes containing a small particle size were successfully developed, and high monomer conversion was demonstrated. These properties are desirable in an industrial setting, which targets high space-time efficiency, and applicability since the latex functions as a final product. Four selected latexes consisting of various monomer compositions were subjected to further investigation in **Chapter 5**. The latexes were colloiddally stable after 11 months of storage at 4 °C according to visual assessment and DLS measurement. After film formation and UV curing, stiff freestanding films were obtained. The tensile properties could be modified by controlling the UV irradiation time. Furthermore, the latex containing 2OA showed promise as an oil and water barrier film for paper applications. In general, cross-linking resulted in drastic increases in solvent resistance, hardness, and blocking resistance of the films applied on a substrate. For some films containing more hydrophobic monomers, water droplets applied on the film showed a high contact

angle. These results support the promise as potential water or oil barrier films. Composites of the latex with cellulose nanocrystals (CNC) were also investigated. The resulting films exhibited drastically increased tensile properties and the formation of a layered cellulose structure was observed in SEM. At the same time, water resistance of the composite was greatly improved compared to pure CNC. The composites could serve as potential gas barrier films in food packaging or electronics.

Using the latex synthesis procedure developed in chapter 4, the polymerization of the vanillin derived MEV was investigated in **Chapter 6**. Latexes containing aldehyde side group functionality were successfully produced. After addition of tris(2-aminoethyl)amine (TREN) as the cross-linker, the latex was casted and dried, resulting in cross-linked films. The latex films were compared to a similar polymer produced via solution polymerization, and cross-linked using the same cross-linker. Since cross-linking proceeds via imine formation, the resulting polymers are cross-linked with thermally reversible covalent bonds and thus can be characterized as vitrimers. Both vitrimers showed rapid stress relaxation at temperatures between 110 and 150 °C with corresponding activation energies of 57 and 64 kJ/mol for the solution and latex vitrimer, respectively. Furthermore, a strong influence of the amount of TREN in the solution vitrimer on the activation energy was observed. This is related to the amount of imine cross-links. A lower concentration of imine groups reduces the likelihood of bond exchange and thus increased the activation energy. The creep recovery of the vitrimers was evaluated, and both showed near complete recovery (though with a retardation) after being subjected to a stress of 0.28 MPa for 5 minutes. Both vitrimers could be recycled. However, the solution polymer showed no significant decrease in tensile properties after 3 cycles, whereas the latex vitrimer could not retain the same mechanical performance after more than one cycle. This could possibly be related to the formation of permanent cross-links and the presence of a phase separated network as a result of the block copolymer structure in the latex vitrimer.

In this thesis, the use of functional and biobased monomers for the production of water-borne acrylic latexes was thoroughly explored. Stable latexes with a good solid content can be obtained by the RAFT PISA method that are suitable for application as films or coatings. Further in-depth research on their behavior as barrier films, composites, or in formulations holds potential according to the results described in this thesis.