Diploma thesis

Group Transfer Polymerization for dental application

carried out at the

Institute of Applied Synthetic Chemistry

at **Technische Universität Wien**

under supervision of

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and

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by

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Abstract

Group Transfer Polymerization (GTP) was first discovered in the 1980s by DuPont and used to synthesize acrylic block copolymers in solution at moderate temperatures. It is a living polymerization technique using mainly 1-methoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (MTS) as the initiator in combination with different catalysts like Brønsted acids. Generally, such controlled polymerization mechanism leads, when used with difunctional monomers in bulk, to very homogeneous networks with improved mechanical properties. These improved properties lead to various possible applications in photopolymerizable systems as well as two-component systems (2K-system) for dental materials.

The aim of this work was to implement the usually solvent based GTP into light or 2K activated methacrylic bulk systems used in dental materials. In order to get an overview over the properties of different catalysts, a selection of literature known catalysts was used in experiments with different monomer systems. An iodonium aluminate salt, which is commonly used for cationic photopolymerization, showed remarkably high reactivity upon irradiation with UV-light when utilized as GTP catalyst.

For the 2K-system several initiating methods were screened, and the very promising in-situ method appeared to be a very potent tool to synthesize polymers with very low PDI in a controlled fashion.

In various experiments the influence of protic groups was investigated. Furthermore, specimens of non-protic monomers were prepared, to compare the mechanical properties of GTP polymerized materials with radically polymerized samples.

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Kurzfassung

Gruppentransferpolymerisation (GTP) wurde erstmals in den 1980er Jahren von DuPont entdeckt und zur Synthese von Acryl-Blockcopolymeren in Lösung bei moderaten Temperaturen verwendet. Es handelt sich um eine lebende Polymerisationstechnik, bei der hauptsächlich 1-Methoxy-1-(trimethylsiloxy)-2-methylprop-1-en (MTS) als Initiator in Kombination mit verschiedenen Katalysatoren, wie Brønsted-Säuren verwendet wird. Generell führen solche kontrollierten Polymerisationsmechanismen bei Verwendung von difunktionellen Monomeren in Masse zu sehr homogenen Netzwerken mit sehr guten mechanischen Eigenschaften. Diese verbesserten Eigenschaften ermöglichen verschiedene Anwendungsmöglichkeiten in photopolymerisierbaren Systemen sowie Zweikomponentensystemen (2K-System) für Dentalmaterialien.

Ziel dieser Arbeit war es, die üblicherweise lösungsmittelbasierte GTP in Licht- oder 2K-aktivierte Methacrylat-Bulk-Systeme zu implementieren, die in Dentalmaterialien eingesetzt werden. Um einen Überblick über die Eigenschaften verschiedener Katalysatoren zu erhalten, wurde eine Auswahl von literaturbekannten Katalysatoren in Versuchen mit verschiedenen Monomersystemen eingesetzt. Ein Iodoniumaluminatsalz, das üblicherweise für die kationische Photopolymerisation verwendet wird, zeigte bei der Bestrahlung mit UV-Licht eine bemerkenswert hohe Reaktivität, wenn sie als GTP-Katalysator eingesetzt wurden.

Für das 2K-System wurden verschiedene Initiierungsmethoden untersucht. Die in-situ-Methode erwies sich dabei als ein vielversprechender Weg zur kontrollierten Synthese von Polymeren mit sehr niedrigem PDI.

In verschiedenen Experimenten wurde der Einfluss von protischen Gruppen untersucht. Außerdem wurden Proben mit nicht-protischen Monomeren hergestellt, um die mechanischen Eigenschaften von GTP-polymerisierten Materialien mit radikalisch polymerisierten Proben zu vergleichen.

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Table of Contents

Introduction		12
Objective		23
General Part		24
Summary		87
Experimental Part		91

		Gen.	Exp.
1	**State of the Art**	**13**	
1.1	Initiators	13	
1.2	Catalysts	15	
1.3	Monomers	17	
2	**Two-Component (2K) GTP**	**18**	
2.1	**Linear Polymers**	**18**	
2.1.1	Synthesis of 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS)	19	81
2.1.2	Screening of initiating systems	19	82
2.1.2.1	Reproducibility	21	
2.1.2.2	In situ	21	
2.1.2.3	Brønsted acid	23	
2.1.2.4	Trityl salt	25	
2.1.2.5	Nucleophilic	26	
2.2	**Networks**	**29**	
2.2.1	Screening of initiating systems	29	82
2.2.1.1	In-situ	30	
2.2.1.2	Brønsted acid	31	
2.2.1.3	Trityl salt	32	
2.2.1.4	Nucleophilic	33	
2.2.2	Protic groups	34	82

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2.2.2.1	Synthesis of ethylhexylurethanemethacrylate	34	82
2.2.2.2	Inhibition of protic groups	35	83
2.3	**Thermomechanical tests**	**36**	
2.3.1	DMTA	37	83
2.3.2	Tensile tests	39	84
2.3.3	Density measurements	41	84
3	**Photoinitiated GTP**	**43**	
3.1	**Linear Polymers**	**44**	
3.1.1	Studies with MTS and I-Al	45	84
3.1.2	Reproducibility	47	85
3.1.3	Studies without MTS / without I-Al	51	85
3.1.4	Radical inhibitors	51	85
3.1.5	Storage stability	56	85
3.2	**Networks**	**57**	
3.2.1	Screening of catalysts	57	85
3.2.2	UV-Vis measurements	60	85
3.2.3	UV activity of trityl salt	62	86
3.2.4	Studies without MTS / without I-Al	63	86
3.2.5	Studies with different MTS / I-Al concentration	64	86
3.3	**Thermomechanical tests**	**66**	
3.3.1	Photo-DSC	67	86
3.3.2	DMTA	69	86
3.3.3	Tensile tests	72	86
3.3.4	Density measurements	75	87

Materials and Methods 88

Abbreviations 91

References 93

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Introduction

Oral diseases, such as dental caries, affect more than 3.5 billion people globally and cause major health burdens for the countries they live in. According to the Global Burden of Disease 2017, untreated dental caries in permanent teeth was the most common health condition. Most oral health conditions, however, are preventable and can be treated in their early stages.[1]

A way to treat these diseases is fillings for the afflicted teeth. The most common dental restorative was amalgam due to its easy applicability to the tooth cavity and the low costs while providing high stability. Amalgam is an alloy consisting of about 50% mercury and other metals such as silver, tin and copper. With the rise of better analytical methods, the health risks of high amounts of mercury in amalgam were questioned.[2, 3] The demand for alternatives lead to the development of composite materials, which had to fulfill several properties of the tooth.

In order to understand the requirements for such a material better, the structure of the tooth has to be understood first, which is displayed in Figure 1.

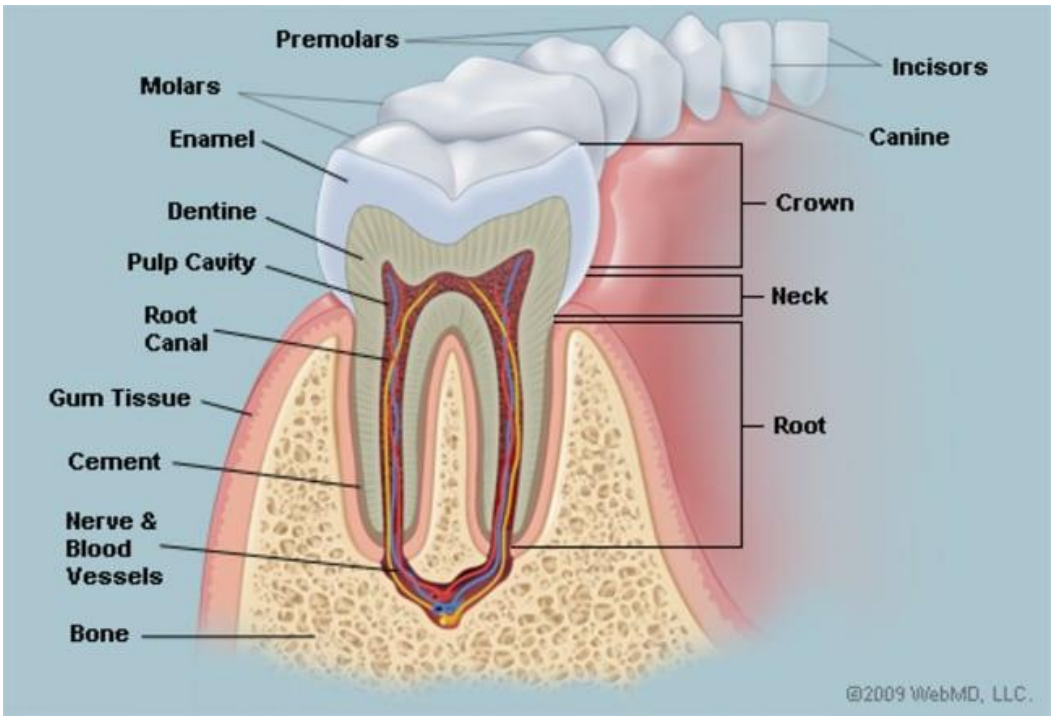

Figure 1: Structure of a tooth[4]

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The enamel layer consists almost 100% of inorganic material, namely hydroxyapatite. However, these hydroxyapatite crystals are embedded in between layers of organic collagen filaments. Although, this structure provides high mechanical stability, it comes with the drawback of susceptibility to acids, primarily lactic acid. The dentine layer, which is anatomically below the enamel, consists of the same material as the enamel. However, it has a higher collagen content and comes with thin pores containing a dentine liquid.[2]

The dental restorative should provide at least the same properties to mimic the enamel and dentine layer. Ideally, it has a lower susceptibility to acids. It is required to be plastically malleable to fit into the cavity and also provide the following:

- high biocompatibility
- good mechanical properties regarding toughness and hardness
- hardening within several minutes
- low cost
- same color as natural teeth

Dental materials

Resin-based dental composites are a very suitable alternative to the previously widely used amalgam fillings. They consist of a polymeric matrix, mainly difunctional methacrylates, and a dispersed reinforcing phase, a radiopaque silica glass. In addition, coupling agents, initiators and stabilizers are components of the composite material.[5]

The organic matrix consists of a mixture of several difunctional monomers. The most common is BisGMA (bisphenol-A-glycidyldimethacrylate) since it provides excellent mechanical properties for the hardened matrix. However, due to its high viscosity and therefore low processability, other monomers are used in the mixture. The mainly used monomers are UDMA (urethanedimethacrylate), TEGDMA (triethyleneglycoldimethacrylate) and D3MA (1,10-decanedioldimethacrylate) due to their lower viscosity and similar mechanical properties. The mentioned monomers are displayed in Figure 2 .[5-8]

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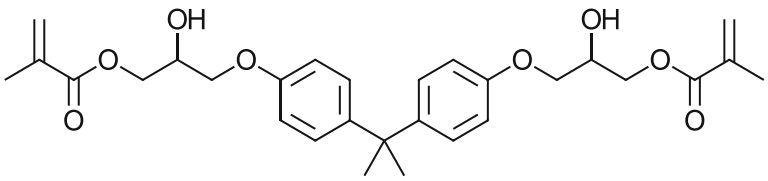
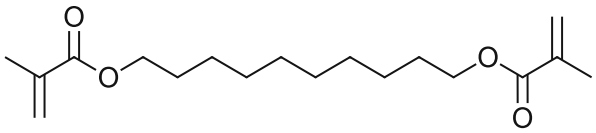
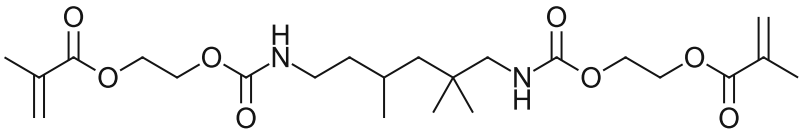


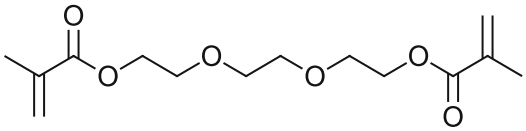
BisGMA



D3MA



UDMA



TEGDMA

Figure 2: Most common monomers for dental composite matrices

However, the properties of dental restorative materials are also greatly influenced by the reinforcing filler materials, which make more than 60wt% of the filling. These properties include radiopacity, mechanical toughness, viscosity and appearance. The commonly used fillers are strontium- and germanium-based silica glasses with a particle size of 1-2 µm and SiO_2 or Si-based oxides with a 10-500 nm particle size. A scheme of a dispersed reinforcing phase in a polymeric matrix is displayed in Figure 3.

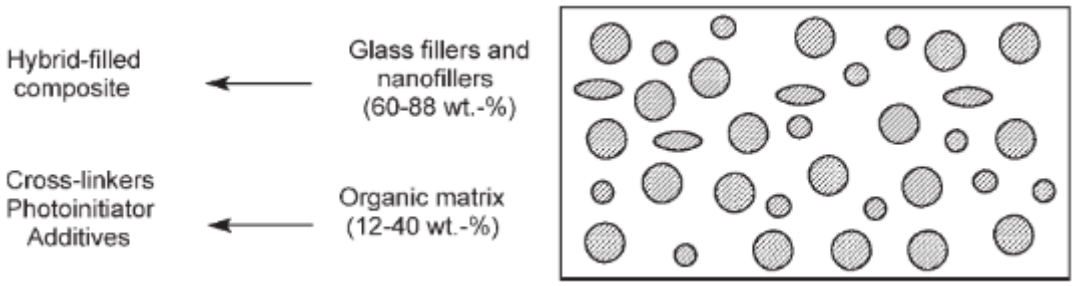


Figure 3: Scheme of a resin-based composite[8]

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Free-radical Photopolymerization

The most common technique to polymerize the organic matrix is via free-radical photopolymerization. In this type of polymerization, a photoinitiator (PI) is brought into an *exciting state* (1) via irradiator with a light source in the first step and forms free radicals (PI·). These radicals add to polymerizable, reactive monomers to form monomer radicals in the *initiation* (2) step. In the *propagation* (3) step, these monomer radicals proceed to add to more monomers and form polymer chains. This chain reaction is then terminated via either recombination of two radicals, or disproportion via hydrogen abstraction in the *termination* (4) step.[9-11] The scheme of the described photopolymerization is depicted in Figure 4.

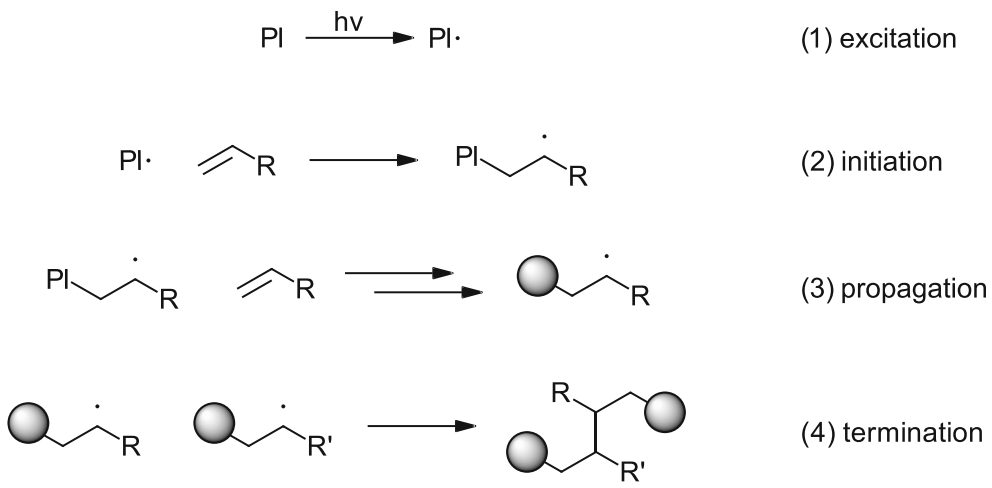

Figure 4: Scheme of free-radical photopolymerization

This polymerization reaction occurs highly rapidly, and the final molecular weight is reached promptly. However, in the presence of oxygen, inhibition occurs via the formation of peroxy radicals that show a drastically lower reactivity. The formation of these radicals is depicted in Figure 5.

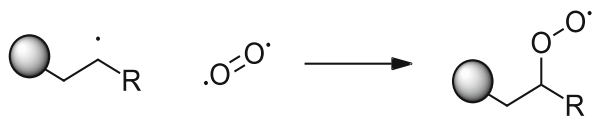

Figure 5: Inhibition via formation of peroxy radicals

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This problem can be tackled by introducing additives such as co-initiators, oxygen barriers, optimizing the photoinitiator, or inerting the atmosphere. However, the oxygen inhibition is mainly a problem for thin coatings due to their high surface exposure.[12]

Initiators

As previously mentioned, the light-sensitive photoinitiator plays a crucial role in the reactivity of a formulation. Furthermore, it is essential that the PI operates at a wavelength that is not harmful to human tissue. In the Jablonsky diagram, the light absorption and the formation of the radicals can be described (Figure 6).

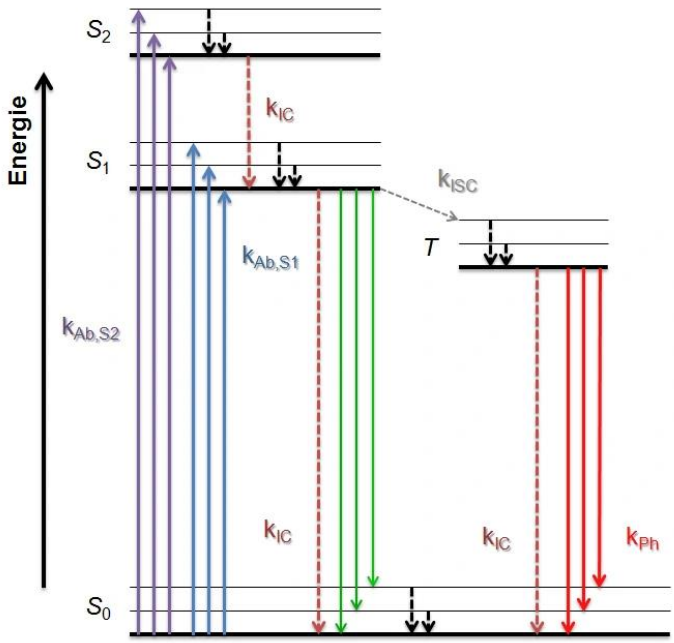

Figure 6: Jablonski diagram[13]

The light energy is absorbed by the photoinitiator and an electron is excited from the S_0 (singlet) to the S_1 or S_2 state. These excited electrons can subsequently undergo either an internal conversion (k_{IC}) to a lower singlet state or an intersystem crossing (k_{ISC}) to a triplet state can occur. This shift from the singlet to the triplet state can lead to the formation of radicals. In this process, two distinctive pathways can be distinguished, which lead to the differentiation of two types of photoinitiators.

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Norrish type I reaction → type I photoinitiator

Norrish type II reaction → type II photoinitiator

Type I photoinitiators usually form radicals via a α-cleavage next to a carbonyl group. The chromophore often is a benzoyl moiety next to the carbonyl group, which determines the optimal wavelength of the photoinitiator. Typical Type I photoinitiators are depicted in Figure 7.[10]

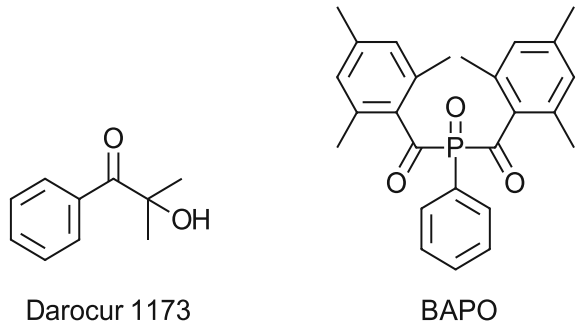

Figure 7: Type I photoinitiators Darocur 1173 and BAPO

The drawback of these photoinitiators is their poor absorption in higher wavelengths above 400 nm, which is why the development of germanium-based initiators was a breakthrough. A Type I initiator widely used in dental materials is Ivocerin, whose cleavage is depicted in Figure 8.[14]

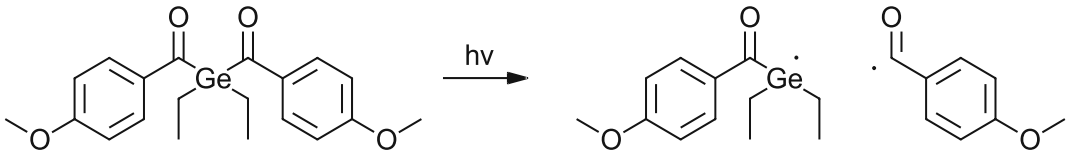

Figure 8: α-cleavage of Ivocerin

Type II photoinitiators, however, do not cleave upon irradiation with light. They react with a co-initiator and form radicals that way via electron transfer or H-abstraction. This bimolecular mechanism is slower than the unimolecular Type I mechanism. Examples of such Type II initiators are ketones in combination with tertiary amines that function as proton donors. The mechanism of the initiation is depicted in Figure 9.[15]

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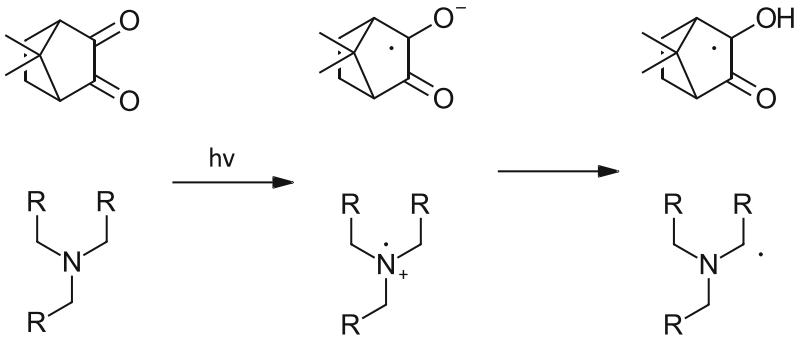

Figure 9: Mechanism of Norrish type II initiators

Group Transfer Polymerization

The so far mentioned free-radical photopolymerization has, despite all its advantages, also the drawback of not providing a controlled, living polymerization. The technique gives poor control over the length and structure of the resulting polymer chains. However, the structure and especially the homogeneity of the polymer network is decisive for the mechanical properties. It was shown that polymer networks prepared via addition-fragmentation chain transfer (AFCT) polymerization have excellent mechanical properties (e.g., high tensile strength and impact resistance) due to the homogeneous structure of the network.[16] This property leads to growing interest in living polymerization techniques. However, the living polymerization technique of Group Transfer Polymerization, despite being developed in the early 1980s, was not investigated deeply and to its full potential.

History

Group Transfer Polymerization (GTP) was first discovered at DuPont as an alternative new living polymerization technique to achieve (meth)acrylic polymers with narrow polydispersity and controlled structures. The driving force for the GTP development was the possibility of having a living polymerization at ambient temperatures and saving costs by not having to cool reaction vessels to -80 °C. [17, 18]

In early attempts, it was discovered that a repetitive Mukaiyama reaction occurs when adding a silyl ketene acetal (SKA) to an activated double bond such as methylmethacrylate (MMA) in the presence of a Lewis acid catalyst, such as $ZnBr_2$. The classic Mukaiyama reaction is depicted in Figure 10.[19, 20]

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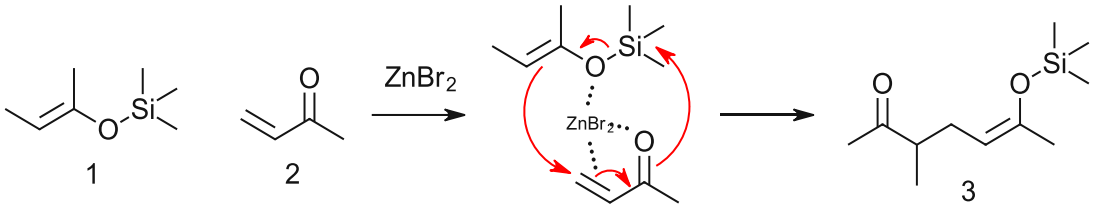

Figure 10: Scheme of the Mukaiyama reaction

The SKA (1) reacts with an activated double bond (2) to form a reactive complex with the Lewis acid. This leads to the addition reaction and the adduct (3) is obtained. Since 3 is structurally similar to 1, the reaction can occur repetitively when more of the monomer is added. In early experiments, this knowledge was used to polymerize (meth)acrylates with $ZnBr_2$ and a SKA. The polymerization reaction is depicted in Figure 11.

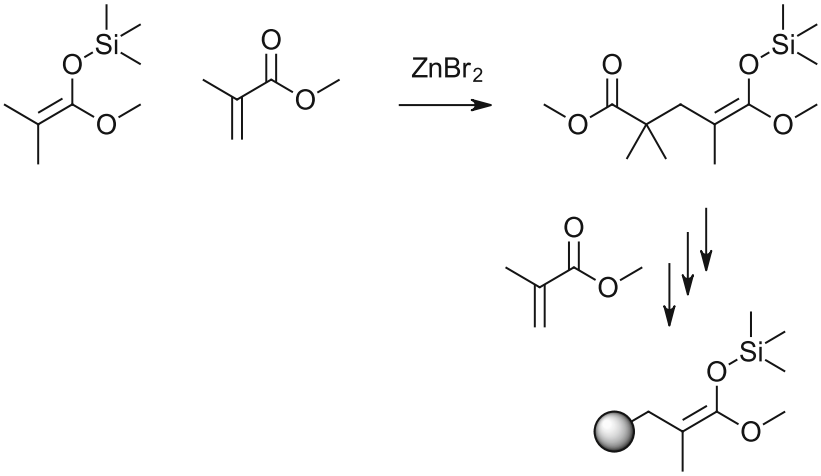

Figure 11: Scheme of the repetitive Mukaiyama reaction

This reaction made it possible to obtain PMMA with a low polydispersity and, because the ratio of SKA to monomer determined the molecular weight, also a defined structure. In further investigations of the new and successful technique, different catalysts were tested, as well as initiators and monomers.[17] The variety of possible catalysts for specific monomers is steadily growing and constant improvements are made. Lewis acid catalysts are the most common ones, although they require a high catalyst loading of 10-20mol% referring to the monomer. Alternatives were investigated in that field and it was found, that nucleophilic catalysts such as tetrabutylammonium salts of CN^- and F^- can catalyze the polymerization in much lower concentrations of 0.1mol% relative to the initiator, which

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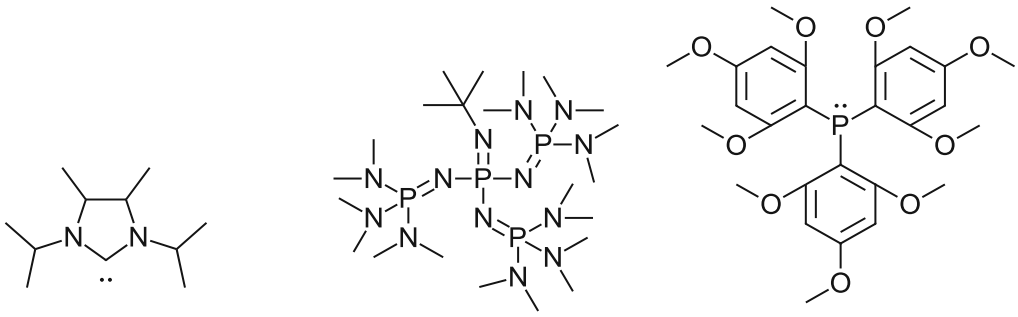
is about $10x10^{-6}$mol% referring to the monomer.[21, 22] However, the mechanism of the polymerization reaction changes, depending on which catalyst is used.

Forms of initiation

Organocatalysts bring several advantages over conventional inorganic catalysts, namely a higher tolerance against oxygen and more tuneable catalytic activity by changing the structure and lowering toxicity.[18, 23] Recent research in potent organocatalysts revealed that Group Transfer Polymerization can be initiated in different ways, each with a different polymerization mechanism. These catalysts can be roughly categorized into the following groups: Lewis bases and Lewis acids (trityl-borates/aluminates, Brønsted acids and nucleophilic catalysts).[24]

Although Lewis base catalysts (Figure 12) perform well in GTP, a much deeper investigation of Lewis acids has been made (Figure 13).[25]



NHC (N-hetrocyclic carbene) Phosphazene base Phosphine

Figure 12: Lewis base catalysts for GTP[18]

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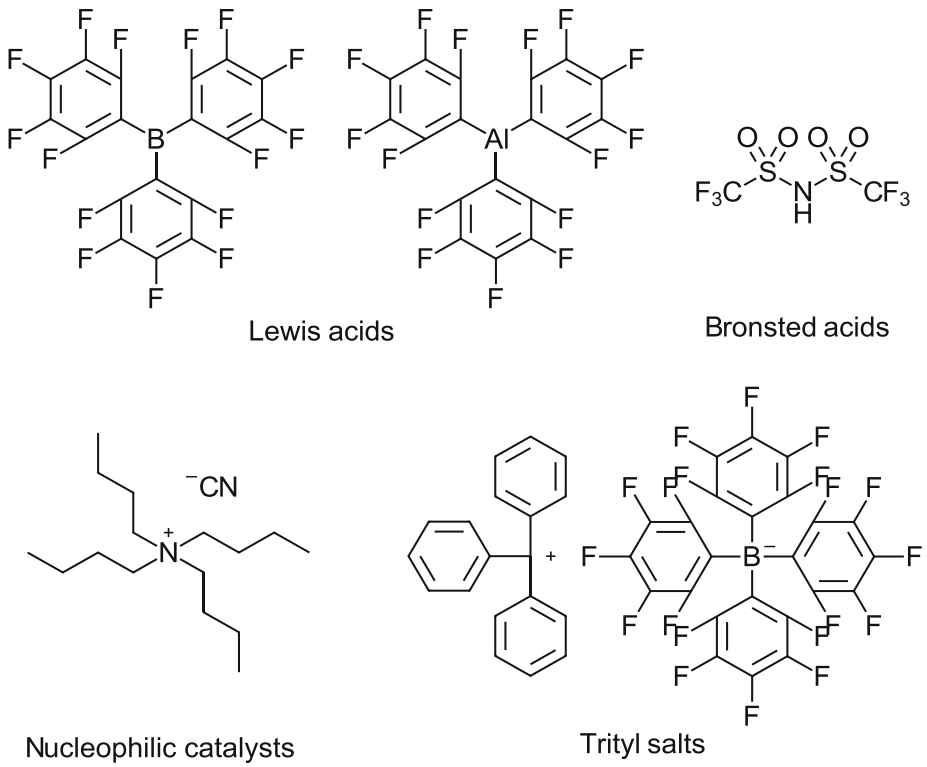

Figure 13: Lewis acid catalysts for GTP[18, 22, 26-28]

Although, each type of catalyst leads to a unique polymerization mechanism, they all ensure a living polymerization and have in common that the repetitive Mukaiyama reaction is performed during the propagation. This control over the chain-growth allows to synthesize polymers with very narrow polydispersity, and if conducted with difunctional monomers, the formed networks should be very homogeneous because of the controlled polymerization.[22]

GTP in bulk and GTP in solvents

Most investigations, however, targeted Group Transfer Polymerization of monofunctional monomers in solvent polymerization. For dental applications, difunctional monomers are used, and they are always polymerized in bulk. Group Transfer Polymerization in bulk is, so far, only reported by a few research groups yet and very poorly investigated. [29, 30] The group of *Patrickios et al.* describes the polymerization of an aminomethacrylate with a SKA and a bibenzoate catalyst displayed in Figure 14.

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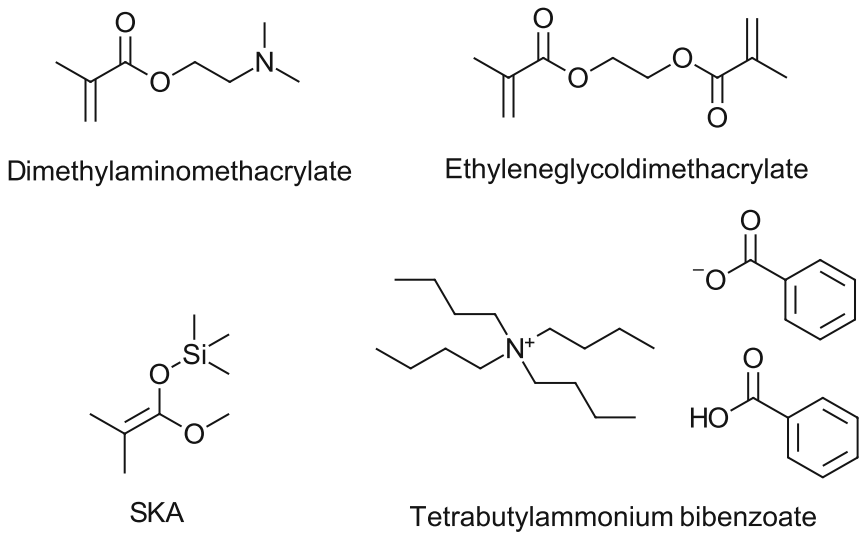

Figure 14: Bulk GTP of Patrickios et al.

This system showed great reactivity and a significant temperature increase 2 min after mixing all components. Although polydispersity of the linear polymers was higher than expected from a living polymerization method, it worked very well for the crosslinked polymers.

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Objective

This thesis aims to investigate the Group Transfer Polymerization (GTP) in bulk, with an emphasis on the application in dental materials. The promising results in previous research on living polymerization techniques causing very tough polymers because of the homogeneous network formation led to the interest in GTP. Since GTP in bulk is very poorly investigated yet, it could be of great potential for such polymers. In this regard, especially common dental monomers should be highlighted concerning their behavior when polymerized via GTP.

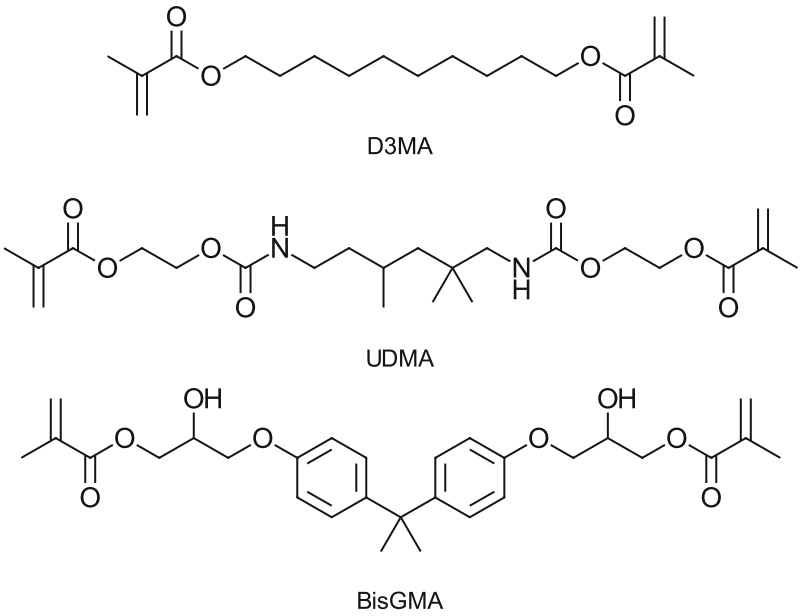

Figure 15: Common dimethacrylates used for dental materials

Therefore, UV-light-initiated photopolymerization systems and two-component systems should be examined in detail. These ways of initiation are most used in dental applications, reasoning the emphasis on them. For both initiating systems, suitable catalysts are necessary and should be investigated with high priority. The observed polymerizations should be characterized and compared to monofunctional reference substances, which are polymerized in bulk.

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General Part

1 State of the Art

Chen et al. report detailed research in the field of group transfer polymerization. However, they always perform the polymerization reaction in solvents. Besides that, almost only linear polymers are investigated to allow detailed analytics to characterize the polymers.[18, 22, 24, 25, 27, 31-33]

1.1 Initiators

The silyl ketene acetal (SKA) initiator has a central role in the GTP, since it not only initiates the polymerization, but also is incorporated in the polymer as well. The core structure of the SKA is mostly the same for the different derivatives and is displayed in Figure 16.

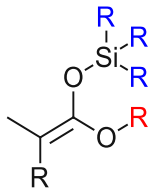

Figure 16: Structure of a silyl ketene acetal (SKA)

Generally, the most common SKA reported in literature is MTS, which has methyl groups for all organic residues. With different catalysts that are either Lewis basic or acidic, MTS can initiate the GTP via different mechanisms. A scheme of the initiation using a nucleophilic catalyst is depicted in Figure 17.

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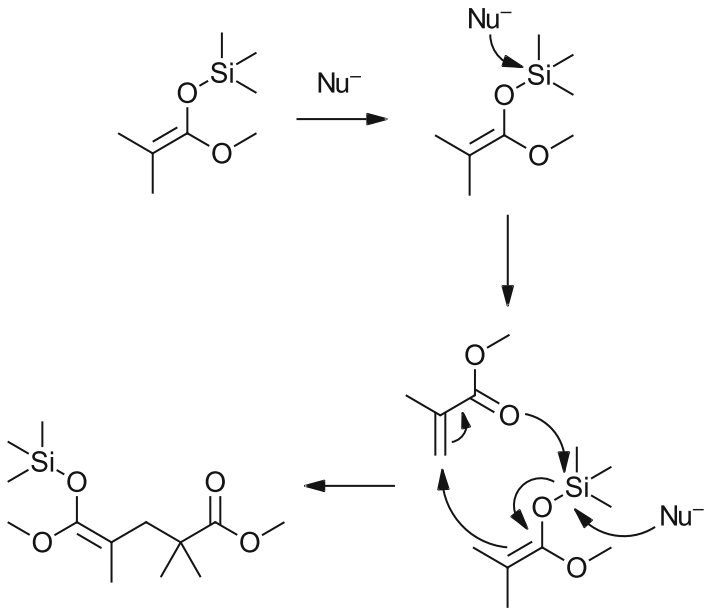

Figure 17: Scheme of the initiation of MTS with a nucleophilic catalyst

The Mukaiyama-Michael reaction occurs between the initiator and the methacrylic monomer in the presence of the nucleophilic catalyst and results in a molecule with the SKA endgroup. This reaction can then proceed repetitively with more monomer, leaving a polymer chain with the SKA endgroup, making it a living polymerization.

As with all living polymerizations, the initiator has roughly the same structure as the living chain ends. This is the case for GTP as well, and the most common initiator is MTS, which has methyl groups for all organic rests, has the methacrylic chain end structure. However, many different derivatives were examined, also including dimeric SKAs. Examples of possible SKA variations are displayed in Figure 18.[18]. The changes of the various R-functionalities impact the ability to initiate a controlled polymerization with high control over the molecular weight. The replacement of smaller groups, such as methyl, with bigger alkyl groups, can reduce the polymerization rate. With the below depicted difunctional SKA derivative, ABA triblock copolymers can be synthesized, and it enables the preparation of end-linked polymer networks.[34]

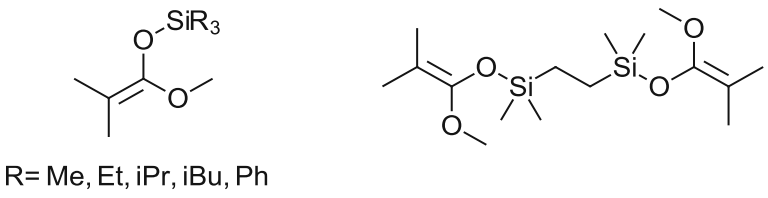

Figure 18: SKA derivatives

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It is also reported that difunctional SKAs and such with different organic residues on the silicon can initiate a highly efficient GTP with MMA in a polar solvent such as DMF without using a catalyst. However, the monofunctional SKA yields polymers with significantly lower PDI than the much faster initiating difunctional SKAs.[31]

1.2 Catalysts

The emphasis in recent developments for catalysts in GTP lies mainly on organocatalysts. As already mentioned, with each type of catalyst, a slightly different polymerization mechanism occurs. In the beginnings of GTP, mainly nucleophilic catalysts, such as tetrabutylammonium salt and tris(dimethylamino)sulfonium cation were used. The reason was that the first proposed mechanisms considered nucleophilic initiation via an associative mechanism. However, widely used catalysts are nowadays are tetrabutylammonium bibenzoate,[29, 30] and trityl tetrakis(pentafluorophenyl)borate displayed in Figure 19.

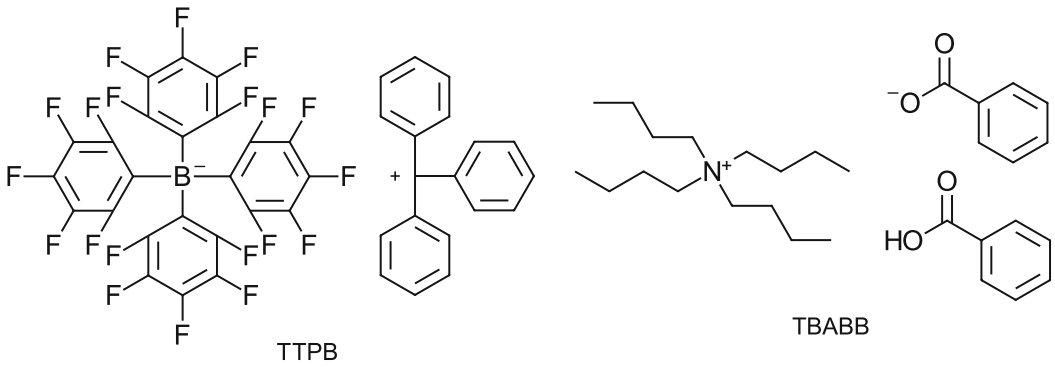

Figure 19: Common catalysts in GTP

In the mechanism of the borate catalyst, the triphenylmethyl cation abstracts a hydrogen atom, causing two SKA molecules to form a dimer, which promotes the polymerization of methacrylic monomers. The SiR_3-group migrates each cycle to the incoming monomer, enabling the addition of the monomer to the chain in a Mukaiyama-Michael type reaction.

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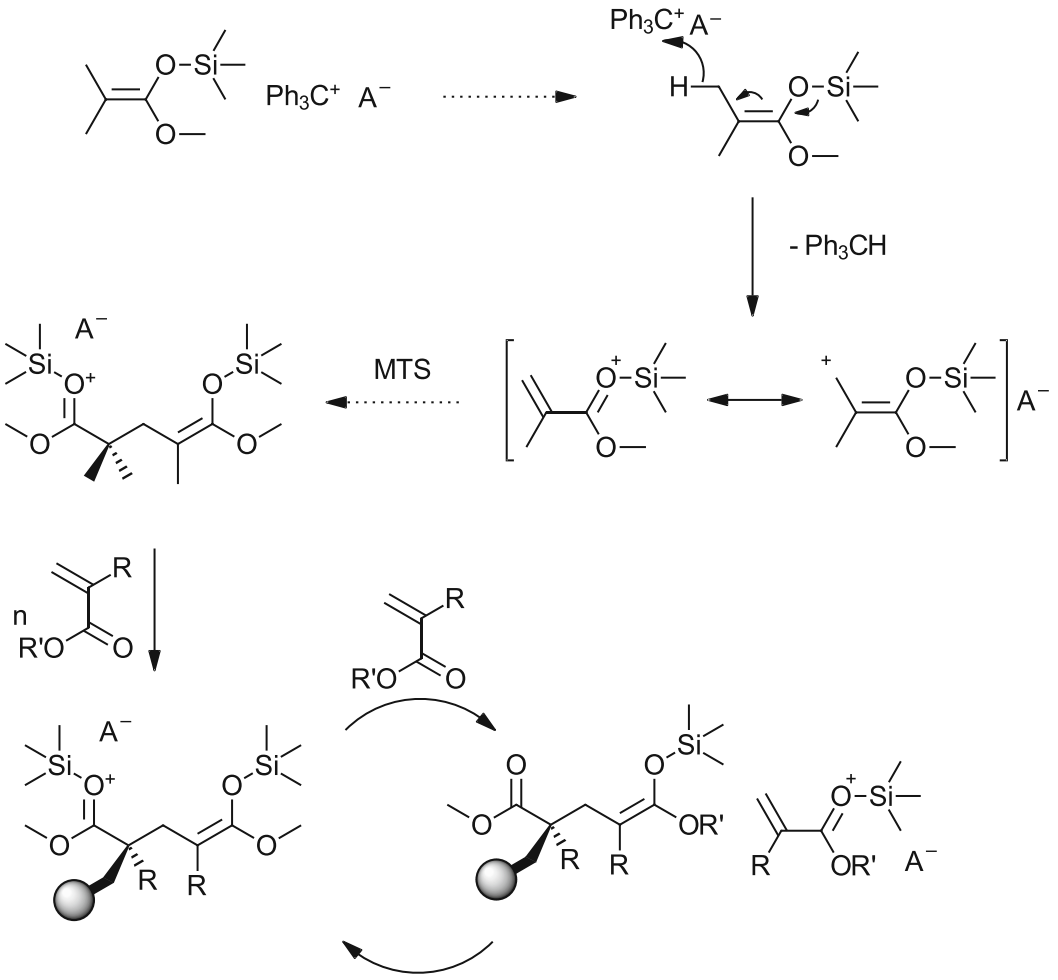

The bibenzoate catalyst is mainly reported in context with GTP in bulk because of its slightly lower reactivity relatively to the more nucleophilic cyanide or fluoride salts and the ability to produce crosslinked methacrylic polymers. However, the borate catalyst is reported to promote the polymerization of several different monomer types, including methylene-butyrolactones, MMA, and other methacrylates, yielding polymers with very narrow molecular weight distributions a variety of different polymer architectures, the most common one being block copolymers of methacrylic monomers. The controlled mechanism also enables more advanced approaches and comes up to a mark for different types of star-shaped polymer networks. Also, other basic catalysts are reported, such as N-heterocyclic carbenes. They are part of the third generation of catalysts developed for the GTP. [34-38]

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1.3 Monomers

The monomers that have been investigated include mainly methacrylates, acrylates, acrylamides, and methylenebutyrolactones (Figure 20)[22, 39, 40]. The choice of the monomer, however, requires a unique initiator with a similar structure. That makes the choice of monomer and initiator always linked together. It is reported that monomers bearing active hydrogens are inhibiting the GTP and produce no polymers when the concentration is higher than the concentration of the initiator. On the other side, the GTP is inert to various functional groups on the monomers, such as allyl, sorbyl, and glycidyl groups. Very little investigation took place on difunctional monomers in GTP, except for *Patrickios et al.* who investigated difunctional dimethacrylates, which were used to randomly crosslink a network.[36]

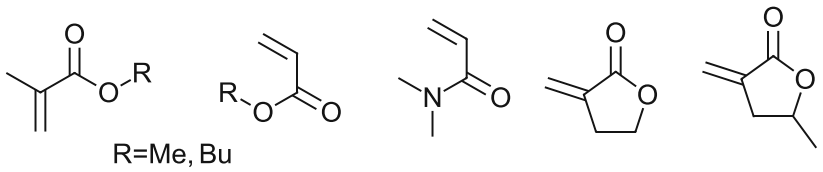

Figure 20: Monomers for GTP

The preferred temperature range for GTP varies highly on the type of catalyst used. However, it can be said that methacrylates are primarily polymerized between 0 °C and 50 °C, which makes it very attractive as the polymerization can be conducted at room temperature. Typically, the polymerization rate is very fast and can be controlled by the addition of monomer. This is only possible when a solvent, typically THF or dichloromethane, is used. When polymerizing in bulk, the polymerization heat cannot be controlled via the addition of monomer, but roughly via the concentration of initiatior.[29, 30, 41]

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2 Two-Component (2K) GTP

Group Transfer Polymerization (GTP) of methacrylic monomers is reported to yield polymers with very defined molecular weight and PDI's below 1,2. The reason lies within the living nature of the polymerization mechanism, which enables a very controlled polymerization. However, most literature reports experiments performed in solution as a 2K system. The catalyst is dissolved in monomer and solvent, and in a separate vial, the initiator is dissolved in the same solvent. Then the solutions are mixed, and the polymerization starts on its own at room temperature. In this work, the GTP as a 2K system is investigated in bulk, where catalyst and initiator are only dissolved in the monomer, which is then mixed.

2.1 Linear Polymers

The principle of 2K polymerization systems is depicted in Figure 21. In separate vials, monomers and initiator on the one hand, and monomers and catalyst, on the other hand, are mixed and dissolved. These formulations are stable and do not polymerize. However, when combining these formulations, after a specific time determined by the concentration of initiator or catalyst, the polymerization reaction starts.

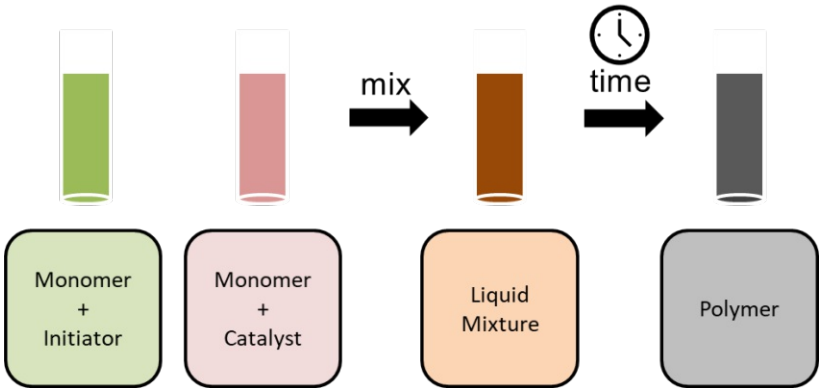

Figure 21: Scheme of the principle of a 2K system in bulk

In these experiments, butylmethacrylate (BMA) was chosen as the monomer. The choice for the initiator fell to 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS), which is the most commonly used initiator for methacrylates reported in literature and shows a very high reactivity because of its little steric hindrance caused by the unbulky methyl groups on the silicon.[31] The monomer used for these experiments is depicted together with the initiator in **Error! Reference source not found.**. Since t he initiator was not commercially available it was synthesized as part of this thesis.

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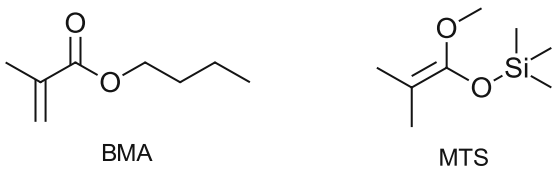

Figure 22: Monomers and initiator used for the screening experiments

2.1.1 Synthesis of 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS)

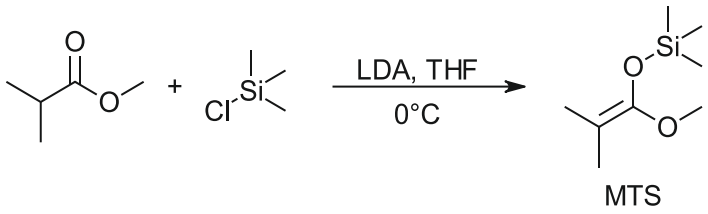

Figure 23: Scheme of the synthesis of MTS

The synthesis of MTS was performed in a straightforward reaction with subsequent purification via distillation. Therefore, methylisobutyrate (1 eq) was converted with trimethylsilylchloride (TMS chloride) (2 eq) in the presence of lithium diisopropylamine (LDA) (1.3 eq) in dry THF under argon atmosphere.[42] After purification via distillation, the product was obtained in a 68% yield as a colorless liquid.

2.1.2 Screening of initiating systems

Initially, a screening was conducted with several different systems that are all reported to initiate the GTP. All four systems are initiating the polymerization via different mechanisms, so a great variety of possibilities for potential 2K systems in bulk was given. The in-situ system creates the initiating species, the SKA, in-situ and has the benefit of lowering the lability of the 2K system by not having the unstable SKA species mixed in the formulation. The trityl borate system was deeply investigated by *Chen et al.* and reported to yield polymers with very narrow PDIs.[18, 22] The Brønsted acid system also creates an initiating silylating species in-situ and was found to be an alternative to Lewis acids in catalyzing the Mukaiyama-Michael reaction.[26, 27, 43] The nucleophilic system is the oldest and most deeply investigated system and was used first as an alternative to the before used inorganic catalysts.[28]

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In total, four different initiation methods (Figure 24) were tested for their reactivity in initiating the 2K polymerization. All reactions for the following experiments were exclusively carried out in a glovebox with dry monomer (< 50 ppm water). Therefore, two formulations were prepared each, one containing the initiator and one containing the catalyst. These two formulations were then mixed and examined for their initiating capability.

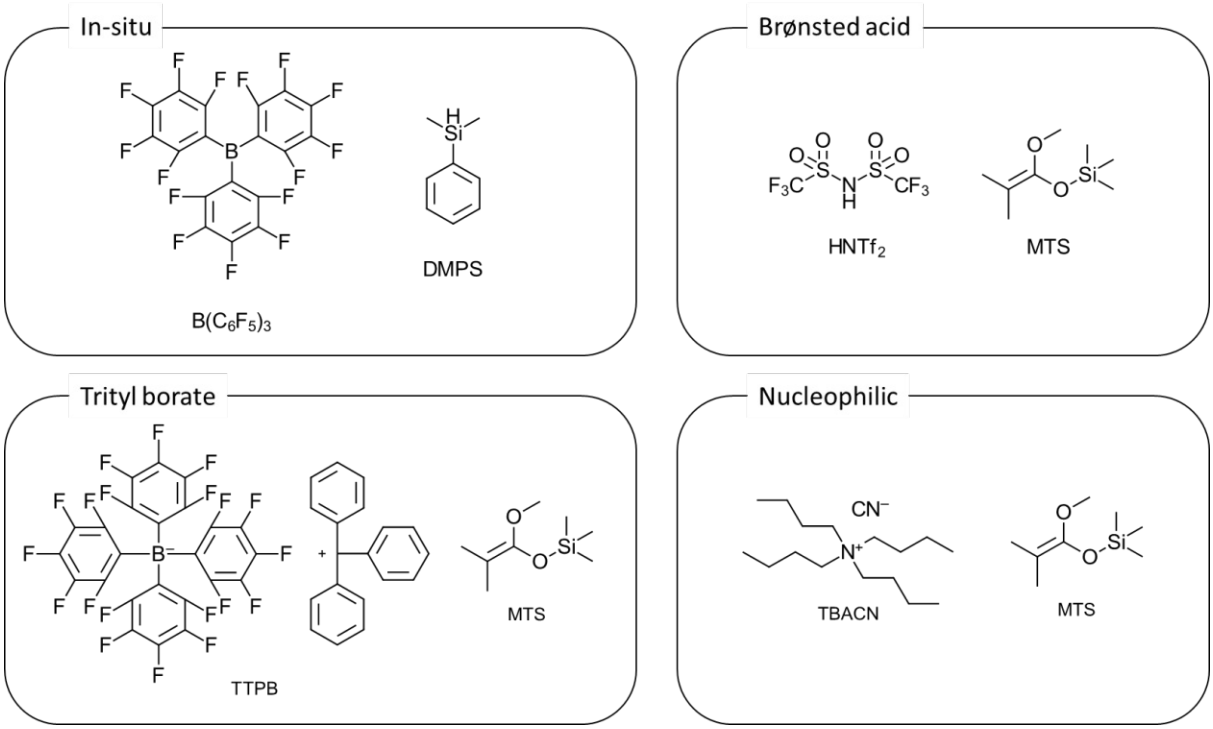

Figure 24: Initiation methods used in the 2K experiments inside a glovebox with BMA

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2.1.2.1 Reproducibility

Because the reproducibility of experiments is an issue with very sensible systems, experiments were conducted for the 2K systems to check if they are reproducible. Therefore, monofunctional butylmethacrylate (BMA) was chosen as the monomer and was polymerized via the trityl borate system with 1mol% MTS initiator and 0.5mol% borate catalyst (TTPB) as three separate formulations. Then, NMR and GPC were measured of the resulting polymers to see if the conversion and the molecular weights, as well as the PDIs, are in the same range. The results of these experiments are shown in Table 1.

Table 1: 2K system reproducibility results with trityl borate system

	DBC_{NMR} (%)	M_n (kDa)	PDI
BMA/1%MTS/0.5%TTPB_1	91	13	2.13
BMA/1%MTS/0.5%TTPB_2	91	10	1.68
BMA/1%MTS/0.5%TTPB_3	91	11	1.79
BMA/1%MTS/0.5%TTPB	91 ± 0	11.3 ± 1.5	1.9 ± 0.2

The linear polymers obtained via the 2K system with the borate catalyst did show excellent reproducibility, for the molecular weight, the PDI and the DBC calculated from NMR. To calculate the DBC via NMR, the two methacrylic H-atoms were used. In that regard, the peaks were integrated before and after polymerization and set into proportion to obtain the conversion. Because the experiment did show a sufficient reproducibility, further experiments were conducted in the glovebox only and with dry monomer to ensure reproducibility.

2.1.2.2 In situ

The initiating system of the in-situ method is depicted in Figure 25 and consists of a borate catalyst and a silane species. In literature, different silanes were already examined; however, dimethylphenylsilane (DMPS) was the best performing one regarding polymerization speed while maintaining a controlled polymerization.[24, 32] The proposed polymerization mechanism for the in-situ initiating system is depicted in Figure 26.

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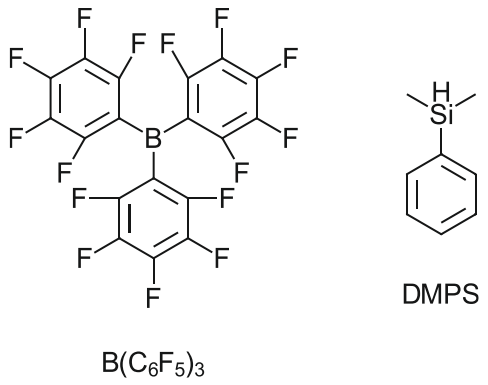

Figure 25: Catalyst and initiator used for the in-situ system

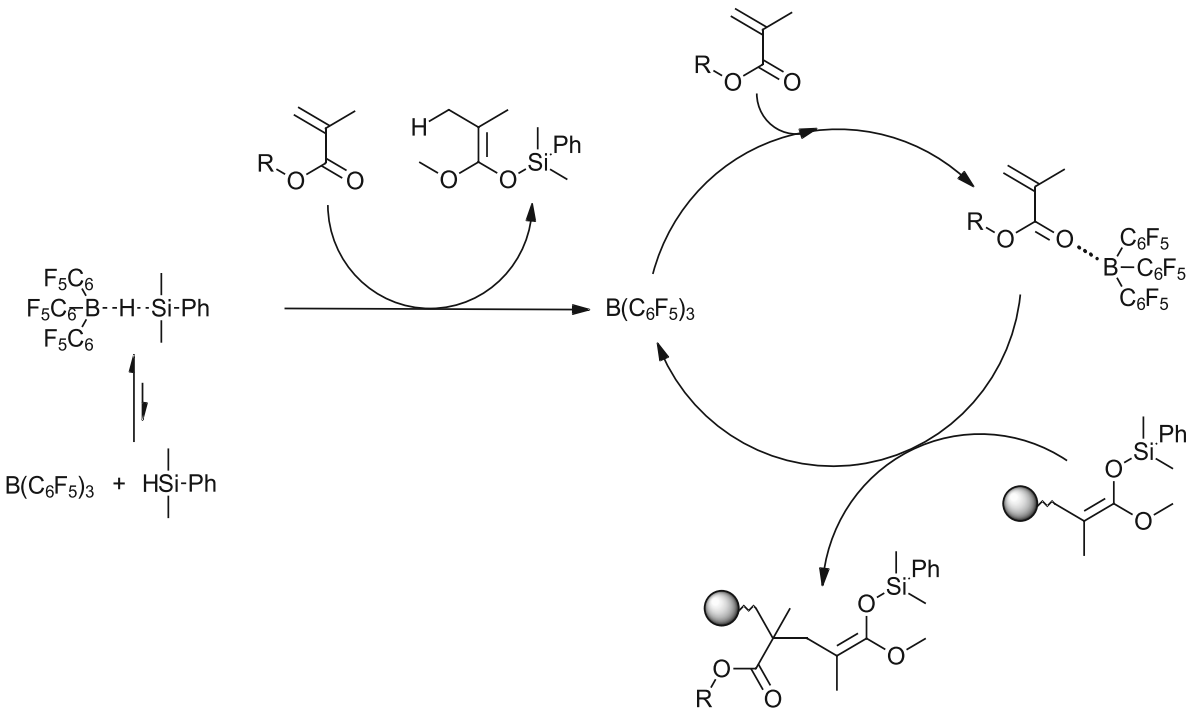

Figure 26: Reaction mechanism for the in-situ system

In this initiating system, the silane hydrolyses the methacrylic double bond of the monomer to form the silylketeneacetal (SKA) in-situ. The borate catalyst activates the incoming monomer, and the SKA initiates the polymerization reaction. A noticeable advantage of this system is creating the SKA species in-situ instead of in advance, because the SKA is a very labile compound compared to the silane.

The formulations were prepared containing BMA, 4mol% silane (DMPS), and 2mol% borate catalyst ($B(C_6F_5)_3$). In Table 2 the GPC and NMR results of the obtained polymer are depicted.

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Table 2: GPC and NMR results of in-situ GTP of BMA with DMPS as initiator and $B(C_6F_5)_3$ as catalyst

M_n (kDa)	14.4
PDI	1.05
DBC_{NMR} (%)	100

The formulations were fully polymerized within 2-3 min, which is a perfectly reasonable time for a 2K system. The pBMA could then be analyzed via GPC and NMR to calculate the DBC, molecular weight, and the molecular weight distribution. As shown, the PDI is below 1.1, which indicates a very controlled polymerization. Especially since the polymerization was completed within 3 minutes with a full conversion, such a low PDI is remarkable. However, with a molecular weight of 14.4 kDa the polymer exhibits longer chains than it would be expected with a concentration of 4mol% DMPS. The controlled polymerization should produce chains of about 3500 kDa if every silane molecule is hydrolyzed to the SKA. This concludes that only a fourth of the silane is actually converted into the initiating SKA, which initiates in a concentration of 1mol% to obtain polymer chains with 14.4 kDa. Nonetheless, the results indicate a very controlled polymerization yielding a polymer with a high conversion, high molecular weights and low PDI.

2.1.2.3 Brønsted acid

Literature reports excellent success with initiating the GTP with Brønsted acids and MTS, which is why this system was tested.[26] An available acid that performs well in literature is $HNTf_2$. For that reason, the below-depicted acid was chosen in combination with MTS (Figure 27). The proposed polymerization mechanism for the Brønsted acid initiating system is displayed in Figure 28.

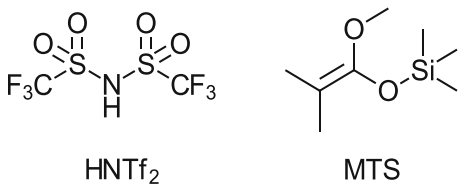

Figure 27: Brønsted acid $HNTf_2$ and initiator MTS

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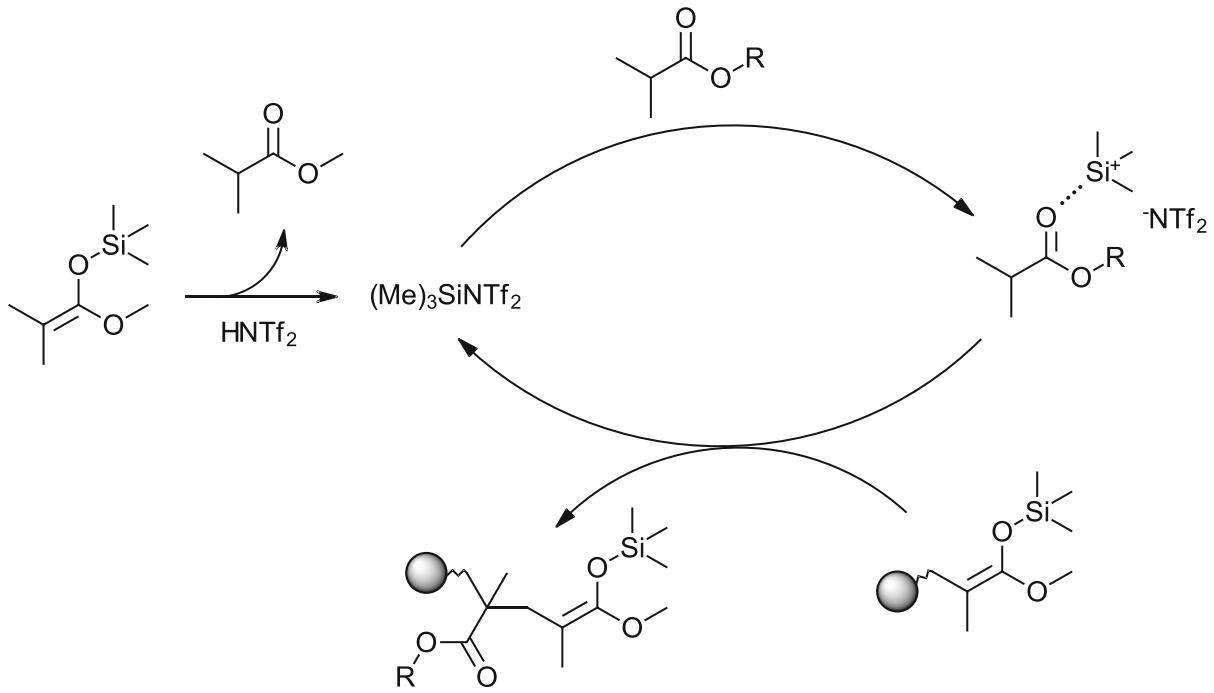

Figure 28: Polymerization mechanism for the Brønsted acid system

$HNTf_2$ forms the silylating agent in-situ with MTS, which can then start the polymerization via activation of the incoming monomer on the carbonyl bond. However, this system can be very vulnerable to protic contaminants, such as urethane or hydroxy groups, since the silylating agent can quickly react with this forming the acid and a silane.[26]

The formulations were prepared containing the monomer BMA, 1mol% MTS, and 0.05mol% $HNTf_2$. No successful polymerization could be observed for this initiating system, yet after one day, a polymerization occurred. However, the obtained polymer was insoluble in the typical solvents for GPC and NMR, so no qualitative analysis was possible.

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2.1.2.4 Trityl salt

The trityl tetrakis(pentafluorophenyl)borate (TTPB) is a commonly used catalyst in literature, especially by *Chen et al.,* and is thought to produce low PDI and high molecular weight polymers.[24, 27] The mechanism for the trityl borate system is shown in Figure 30.

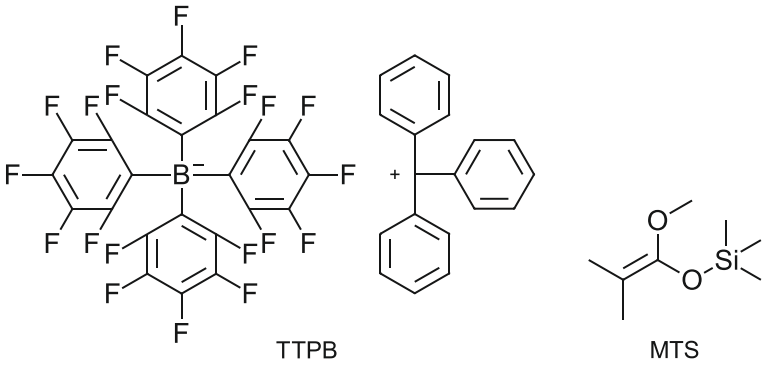

Figure 29: Trityl borate catalyst and initiator MTS

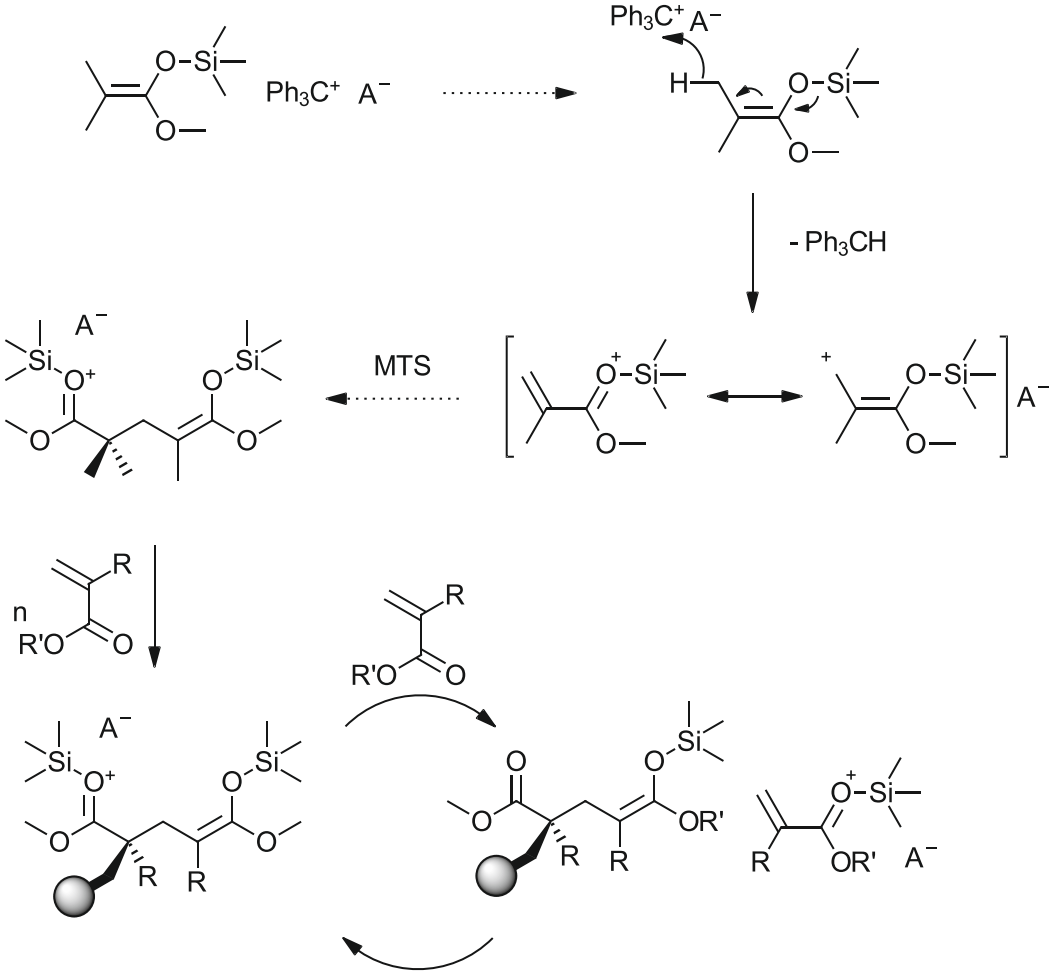

Figure 30: Polymerization mechanism for the trityl salt mechanism

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The triphenylmethyl cation abstracts a hydrogen atom, causing two SKA molecules to form a dimer, promoting the polymerization of methacrylic monomers. The SiR_3-group migrates each cycle to the incoming monomer, enabling the addition of the monomer to the chain in a Mukaiyama-Michael type reaction.

The formulations were prepared containing the monomer BMA, 1mol% MTS, and 0.5mol% borate catalyst (TTPB). In Table 3, the GPC and NMR results of the obtained polymer are displayed.

Table 3: GPC and NMR results of trityl salt initiated GTP of BMA with MTS as initiator and TTPB as the catalyst

M_n (kDa)	11.3
PDI	1.9
DBC_{NMR} (%)	91

The GPC and NMR analysis results of the pBMA show a higher PDI than obtained with the in-situ method. This method seems not to benefit from the polymerization in bulk, since it is reported to produce highly defined polymers in solution. A reason might be the hindrance of the chains to monomer due to diffusion in the already gelled formulation. However, the molecular weight is in the expected order of magnitude since with 1mol% MTS, 14 kDa would be the anticipated weight. The deviation from the expectation can be explained by the high PDI of 1.9, which is likely caused by difficult monomer diffusion.

2.1.2.5 Nucleophilic

In the very first approaches of GTP, inorganic nucleophilic catalysts were used with a SKA to polymerize methacrylic monomers. A very common organic nucleophilic catalyst used in later more advanced approaches was tetrabutylammonium cyanide in combination with the initiator MTS.

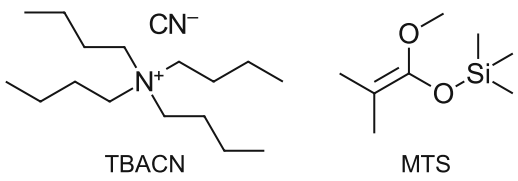

Figure 31: Nucleophilic catalyst and initiator MTS

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The polymerization mechanism for the nucleophilic system is depicted in Figure 32. *Path a* refers to the associative mechanism in which the silyl group stays attached to the propagating polymer, eponymous for the GTP. P*ath b* refers to a later postulated dissociative mechanism, which involves the formation of enolate anions, which are under constant complexation with another SKA molecule.[44]

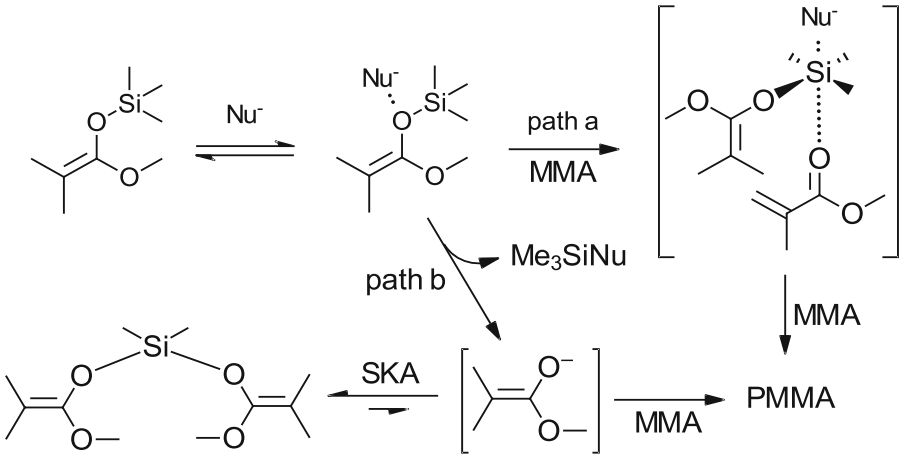

Figure 32: Polymerization mechanism of the nucleophilic system

The formulations were prepared containing the monomer BMA, 1mol% MTS, and 0.5mol% cyanide catalyst (TBACN). In Table 4 the GPC and NMR results of the obtained polymer are displayed.

Table 4: GPC and NMR results of nucleophilic initiated GTP of BMA with the catalyst TBACN and initiator MTS

M_n (kDa)	36
PDI	3.2
DBC_{NMR} (%)	60

BMA polymerizes very quickly (< 10 s) upon mixing in this initiating system. The GPC and NMR results of pBMA indicate a less controlled polymerization since the PDI is significantly higher, which corresponds to the extremely fast polymerization compared to the trityl salt or the in-situ methods. Also, the low DBC is a sign of the polymerization occurring too fast to polymerize all available monomer before gelation.

Since the polymerization speed in this system is an issue because the formulations cannot be adequately mixed before they polymerize, it was also tested to lower the catalyst concentration. Therefore, the MTS concentration was held constant at 1mol%, and the catalyst concentration was

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lowered to $1x10^{-4}$ mol/L, $1x10^{-5}$ mol/L, and $1x10^{-6}$ mol/L. However, the polymerization speed did not slow down, but at $1x10^{-6}$ mol/L, no polymerization was observed anymore. So, it can be assumed that the polymerization speed, in this case, is not affected by the catalyst concentration.

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2.2 Networks

In mind of the application in dental materials, not only monofunctional systems were investigated, but also difunctional monomers forming networks. Therefore, common monomers used in dental fillings were investigated regarding their reactivity in GTP systems. To get an overview, a screening was conducted.

2.2.1 Screening of initiating systems

In the screening conducted with difunctional monomer systems, the same initiating systems as for the monofunctional screening were used. Furthermore, regarding the monomers, UDMA and BisGMA are commonly used difunctional methacrylates for dental application in combination with D3MA and were selected here. Since BisGMA and UDMA both have protic functional groups and it is reported that protic groups can inhibit the GTP, D3MA alone was tested as well. The monomers, as well as the initiating systems, are depicted in Figure 33 and Figure 34.

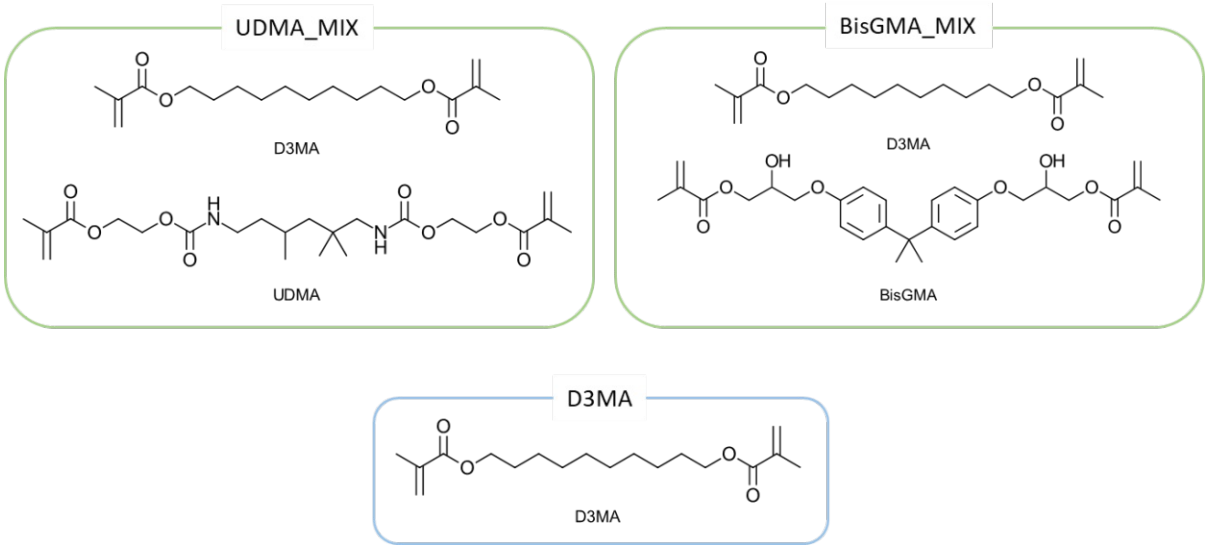

Figure 33: Difunctional monomers used in the screening conducted inside a glovebox

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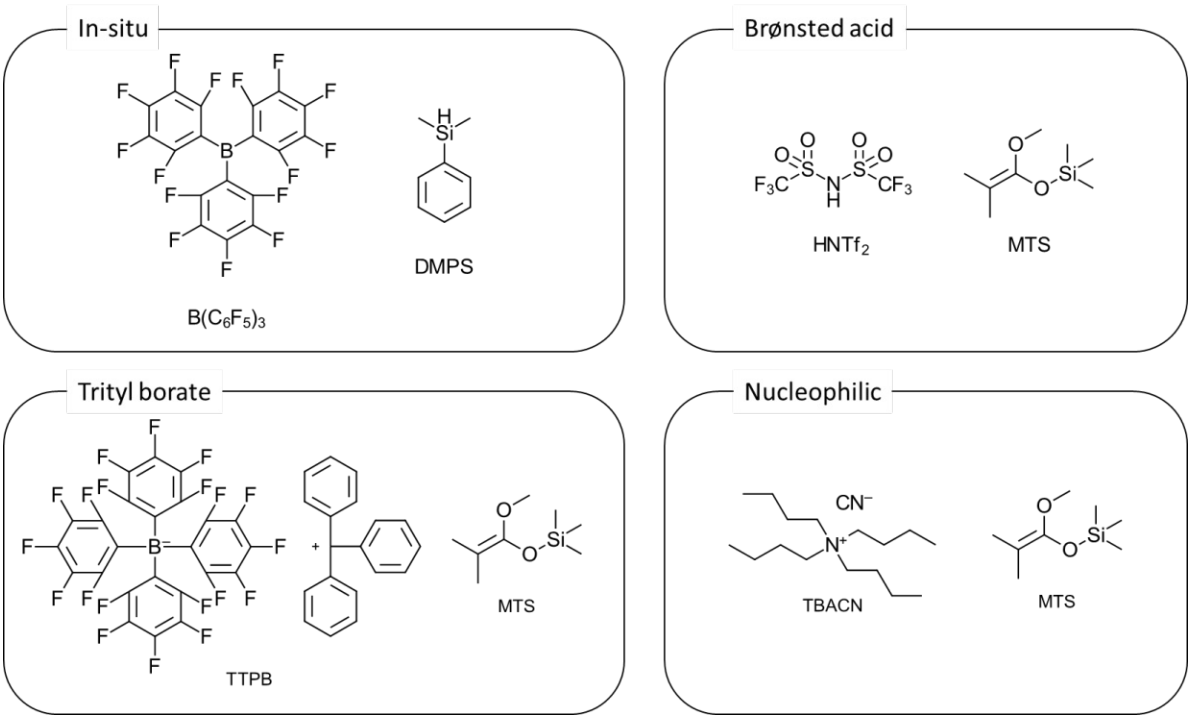

Figure 34: Initiation methods used in the conducted screening using difunctional monomers

In total, four different initiation methods were tested for their reactivity in initiating the 2K polymerization with the three different monomer mixtures. All reactions for the following experiments were exclusively carried out in the glovebox with dry monomers (< 50 ppm water). Therefore, two formulations were prepared each, one containing the initiator and one containing the catalyst. These two formulations were then mixed and examined for their initiating capability.

2.2.1.1 In-situ

The initiator system for the in-situ method is depicted in Figure 35 and tested with the aforementioned difunctional monomer mixtures (Figure 33) with 4mol% DMPS and 2mol% borate catalyst ($B(C_6F_5)_3$) shown in Figure 36. The mechanism of the polymerization was already discussed in detail in chapter 2.1.2.2 (page 21) with BMA as monofunctional monomer.

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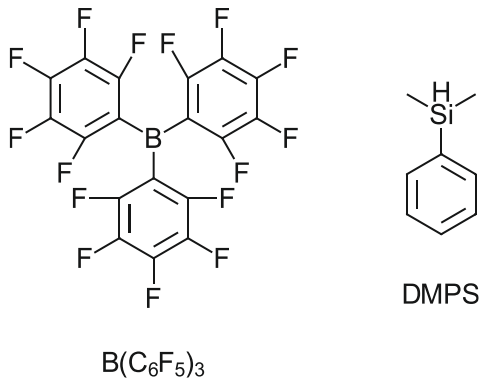

Figure 35:In-situ initiating species

D3MA	UDMA_MIX	BisGMA_MIX
4% DMPS	4% DMPS	4% DMPS
2% $B(C_6F_5)_3$	2% $B(C_6F_5)_3$	2% $B(C_6F_5)_3$

Figure 36: Results of the in-situ experiments with difunctional monomer systems

D3MA polymerized within a concise amount of time (2-3 min.), which is about the same as for the monofunctional BMA. However, the two monomers mixtures with UDMA and BisGMA did not show any polymerization. As a result of the very low PDI of the BMA polymer synthesized with this method, the D3MA network is assumed to be highly homogeneous.

2.2.1.2 Brønsted acid

The initiator system for the Brønsted method is depicted in Figure 37 and was tested with the before mentioned difunctional monomer mixtures (Figure 33) with 1mol% MTS, and 0.05moL% $HNTf_2$ depicted in Figure 38. The mechanism was already discussed in chapter 2.1.2.3 (page 23) with BMA as monofunctional monomer.

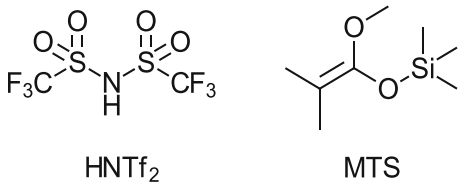

Figure 37: Brønsted acid initiating species

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D3MA	UDMA_MIX	BisGMA_MIX
1% MTS	1% MTS	1% MTS
0.05%$HNTf_2$	0.05%$HNTf_2$	0.05%$HNTf_2$

Figure 38: Results of the Brønsted experiments with difunctional monomer systems

None of the formulations that were prepared were polymerized. Even after raising the concentrations of the initiators to 4% MTS and 0.2% $HNTf_2$, no polymerization was observed, which might be due to the high susceptibility of this mechanism to protic groups. Since this system did not yield polymers with D3MA and BMA as well, it can be argued that, in this case, a solvent is necessary for a successful polymerization.[26]

2.2.1.3 Trityl salt

The initiator system for the method using the trityl salt is depicted in Figure 39 and tested with the aforementioned difunctional monomer mixtures (Figure 33) and 4mol% MTS and 2mol% TTPB (Figure 40). The mechanism of this system was already discussed in detail in chapter 2.1.2.4 (page 25) with BMA as monofunctional monomer.

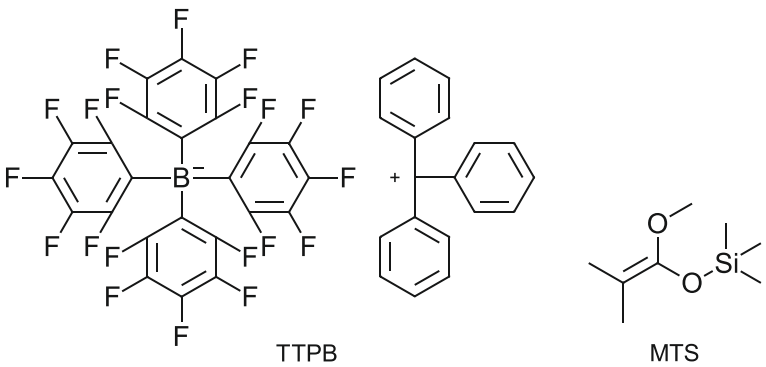

Figure 39: Trityl borate catalyst and initiator MTS

D3MA	UDMA_MIX	BisGMA_MIX
4% MTS	4% MTS	4% MTS
2% TTPB	2% TTPB	2% TTPB

Figure 40: Results of the trityl salt experiments with difunctional monomer systems

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Compared to the monofunctional monomer system, higher concentrations of 4% MTS and 2% TTPB were used to enable a successful polymerization. However, only D3MA did show a polymerization; the two mixtures with UDMA and BisGMA did not polymerize. Even after raising the concentrations to 10% MTS and 5% TTPB no polymerization could be observed.

2.2.1.4 Nucleophilic

The initiator system for the nucleophilic method is depicted in Figure 41 and was tested with the before mentioned difunctional monomer mixtures (Figure 33) and 1mol% MTS and 0.5mol% TBACN (Figure 42). The polymerization mechanism of this system was already discussed in chapter 2.1.2.5 (page 26) with BMA as monofunctional monomer.

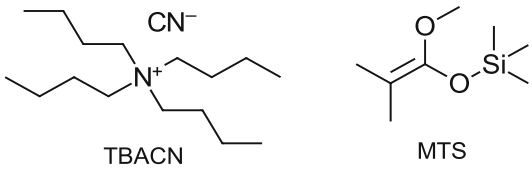

Figure 41: Nucleophilic initiating species

D3MA	UDMA_MIX	BisGMA_MIX
1% MTS	1% MTS	1% MTS
0.5%TBACN	0.5%TBACN	0.5%TBACN

Figure 42: Results of the experiments using the nucleophilic system with difunctional monomers

The same results as for the in-situ and the trityl salt systems were obtained with the nucleophilic approach. D3MA showed a successful polymerization, while the mixtures with UDMA and BisGMA did not show any polymerization, even after raising initiator concentrations to 4% MTS and 2% TBACN.

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2.2.2 Protic groups

The conducted experiments show a clear trend towards the assumption that protic groups inhibit the polymerization via GTP since none of the UDMA or BisGMA mixtures polymerized. Still, in almost every case, the non-protic monomers D3MA and BMA polymerized with the applied systems. The following experiments intend to proof, that the GTP of BMA shows living polymerization behavior and gets inhibited when adding monomers containing urethane or hydroxy groups. Therefore, monofunctional BisGMA and UDMA derivatives hydroxyethylenemethacrylate (HEMA) and ethylhexylurethanemethacrylate (EHUMA) were used. With these monofunctional equivalents, subsequent GPC analysis of the polymers is possible. EHUMA was not commercially available, which is why it was synthesized as a part of this work.

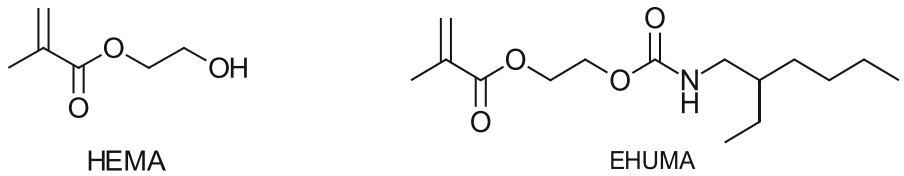

Figure 43: Chemical structure of monofunctional BisGMA and UDMA derivatives HEMA and EHUMA

2.2.2.1 Synthesis of ethylhexylurethanemethacrylate (EHUMA)

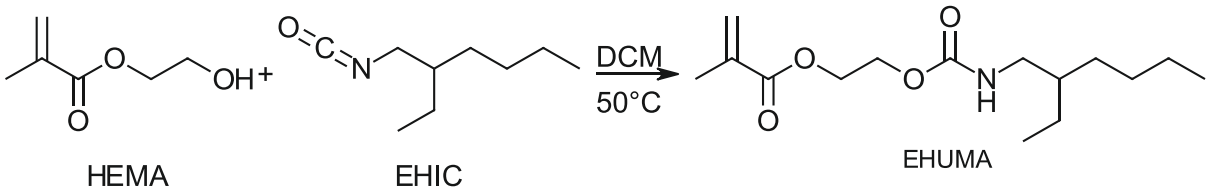

Figure 44: Scheme of the synthesis of ethylhexylurethanedimethacrylate

Hydroxyethylmethacrylate (HEMA) (1eq) and ethylhexylisocyanate (EHIC) (1eq) were introduced to DCM in a flask under argon atmosphere. The reaction was stirred at 50 °C for 2 h. Subsequently, the solvent was evaporated, and the reaction mixture was purified via column chromatography (PE:EE=3:1) and any educts left in the solution were separated.

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2.2.2.2 Inhibition of protic groups

The urethane, as well as the hydroxy groups of UDMA and BisGMA, are assumed to interfere with the GTP of these monomer mixtures. This is why an experimental setup was designed in which monofunctional BMA is polymerized via the very well working in-situ system, and the livingness of the polymerization is confirmed. Subsequently, EHUMA or HEMA are added, which should stop the polymerization and inhibit further polymerization of BMA if the groups are inhibiting the GTP. The workflow of the experiments is depicted in Figure 45.

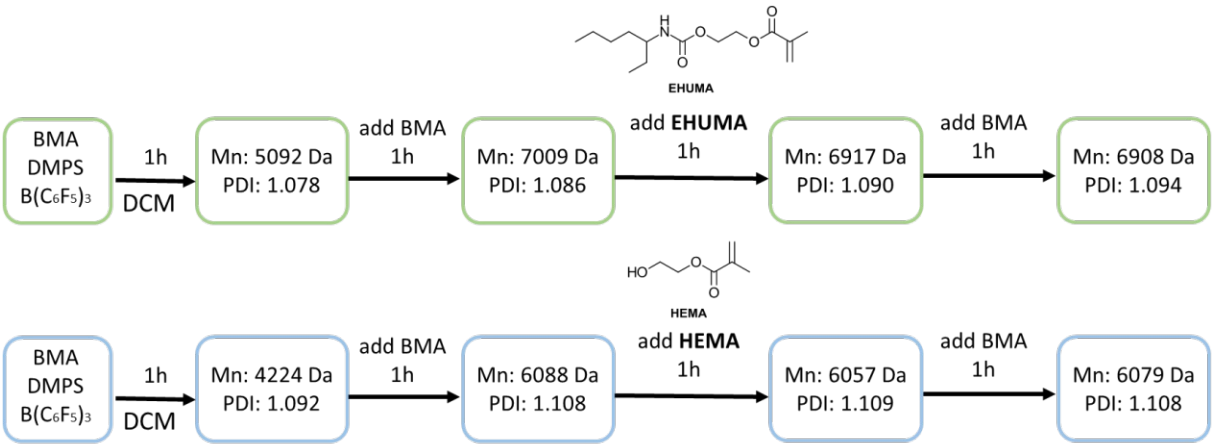

Figure 45: Workflow of the GTP inhibition experiment using EHUMA and HEMA

Therefore, both experiments start with the polymerization of BMA via the in-situ method in a 2 mol/L DCM solution instead of bulk. GPC is measured from the obtained polymers to get a starting value of the molecular weight and the PDI. Then, to prove that the polymerization is a living polymerization, another 0.5eq BMA is added, and after 1h of reaction time, again GPC is measured. The molecular weight increased while maintaining low PDIs. Then in one case, the urethane group containing methacrylate EHUMA is added, while in the other case, the hydroxy group containing methacrylate HEMA is added. Both cases show no further polymerization, even when another 0.5eq BMA is added. EHUMA and HEMA seem to not only not polymerize themselves but also inhibit any further polymerization of BMA, which leads to the conclusion that the urethane and the hydroxy group are inhibiting the polymerization of the formulations via GTP.

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2.3 Thermomechanical tests

As a consequence of chapter 2.2.2 showing that protic groups are inhibiting the GTP, alternatives had to be found for BisGMA and UDMA. Therefore, formulations were prepared inside a glovebox with dried (<50ppm water) non-protic monomers that are depicted in Figure 46 and Table 5.

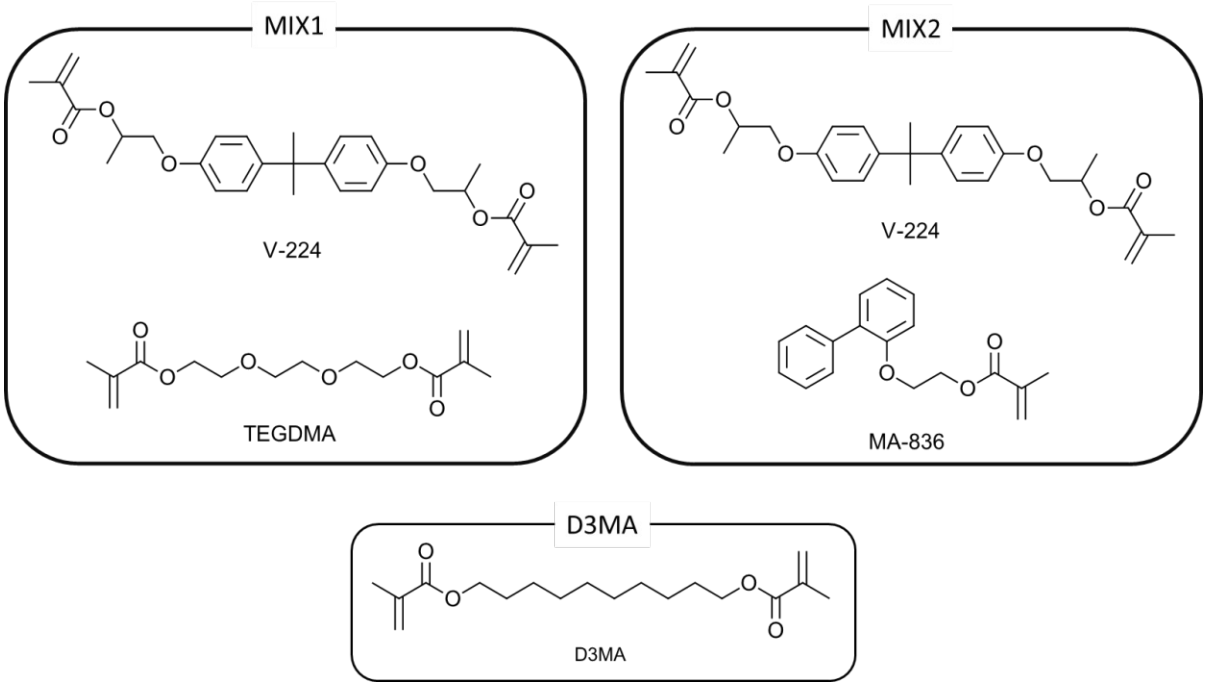

Figure 46: Non-protic monomers used for 2K experiments

V-224 is a derivative of BisGMA without the OH-group, which is it an easy choice. TEGDMA is a common dimethacrylate for dental polymers, and MA-836 is a monofunctional methacrylate with a higher viscosity that leads to proper materials. The mixtures of these monomers depicted in Table 21 were kindly provided by Ivoclar AG.

Table 5: Composition of formulations with non-protic monomers

MIX1		MIX2	
	wt%		wt%
V-224	70	V-224	70
TEGDMA	30	MA-836	30

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Unfortunately, in experiments with MIX1 and MIX2 with the previously described initiating systems, no successful polymerization could be observed with any of the four systems. The same concentrations as for the shown UDMA_MIX and BisGMA_MIX were used. A possible reason for that might be the high viscosity of the formulations and the low solubility of the catalysts.

2.3.1 DMTA

Although the experiments with the MIX1 and MIX2 monomer mixtures were unsuccessful, DMTA specimens using only D3MA as a monomer were prepared. For the specimens, the in-situ method with 4% MTS and 2% DMPS was chosen since it showed excellent results in the previous experiments, obtaining polymers with a narrow PDI of 1.05. All specimens were prepared inside a glovebox. As a 2K reference system, an already established redox polymerization system was chosen (Figure 47).[45] For the reference system 4.3wt% cumene hydroperoxide (CHP), 2.2wt% 1-thioureido-1-hexanone and 0.005wt% $Cu(acac)_2$ were used.

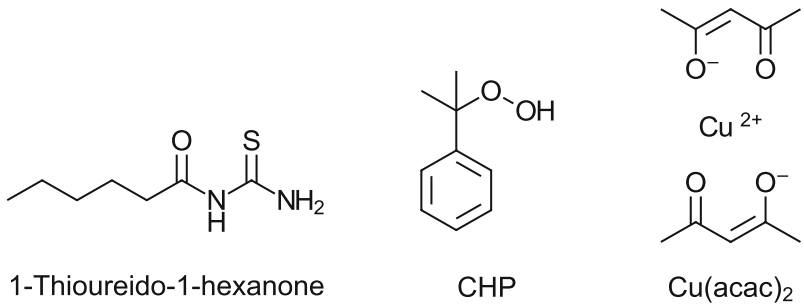

Figure 47: 2K Redox reference system

In order to quantify the success of the polymerization, the double bond conversion of the resulting specimens is depicted in Table 6, which was calculated from ATR-IR measurements of the specimens by integrating the absorption band of the methacrylic C=C stretch at 1640 cm^{-1} of the polymer and the monomer and comparing them.

Table 6: DBC of the specimens polymerized with the in-situ system and the redox system

	DBC (%)
D3MA in-situ	85.0
D3MA redox	80.1

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Interestingly, the DBC of the in-situ polymerized specimen is higher than the redox polymerized sample. The resulting DMTA measurements of the D3MA specimens are depicted in Figure 48 and Figure 49.

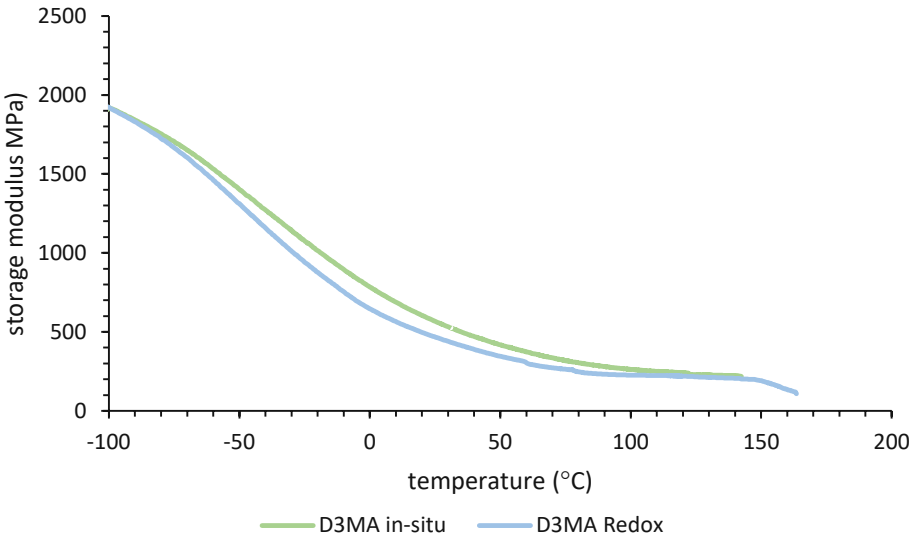

Figure 48: Storage modulus of D3MA in-situ and D3MA Redox

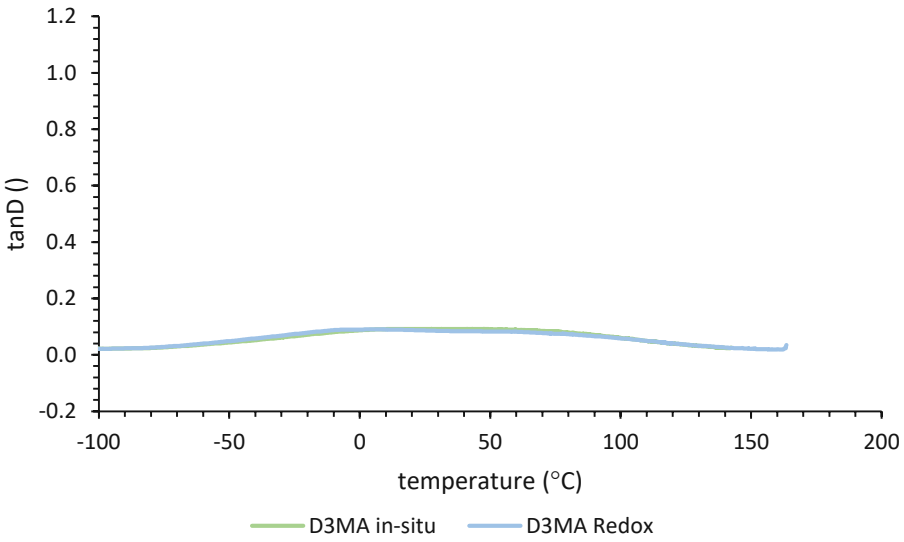

Figure 49: tanD of D3MA in-situ and D3MA Redox

Unfortunately, both specimens broke before reaching their respective T_g's because they were too brittle. Nevertheless, the storage modulus of the GTP and the redox sample is very comparable,

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although the decrease of the storage modulus is not as steep as for the redox sample, which might be due to the slightly higher DBC. Because of the significant similarity of the tanD curves and the storage modulus curves, it can be assumed that the T_g is at very similar temperatures as well.

2.3.2 Tensile tests

Specimen for tensile tests were prepared of D3MA. Therefore, D3MA with 4mol% DMPS and 2mol% $B(C_6F_5)_3$ was mixed inside the glovebox and immediately transferred into the mold for the tensile test specimen. Furthermore, reference specimens with the redox system (Figure 47) were prepared to compare the GTP to free radical polymerization.

The Young's modulus, as well as strain and stress at break, are displayed in the diagrams below.

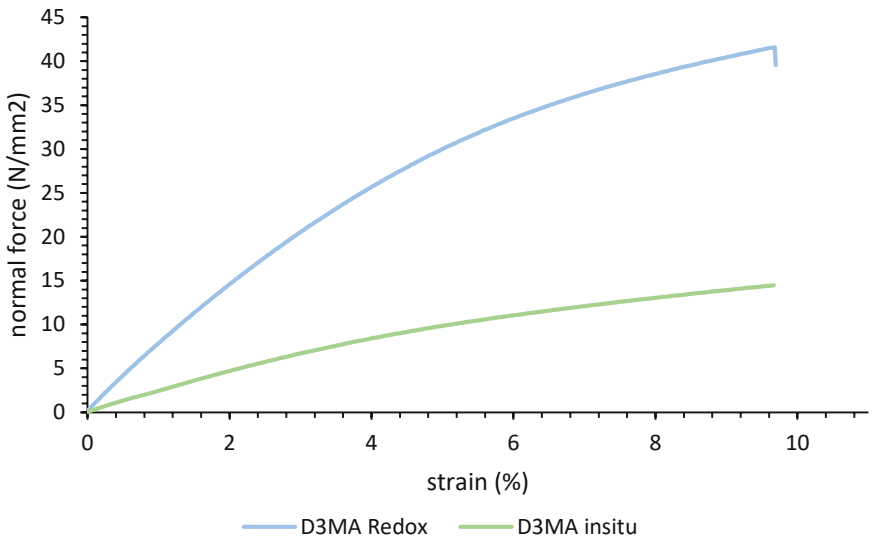

Figure 50: Stress-strain diagram of D3MA Redox in comparison with D3MA in-situ

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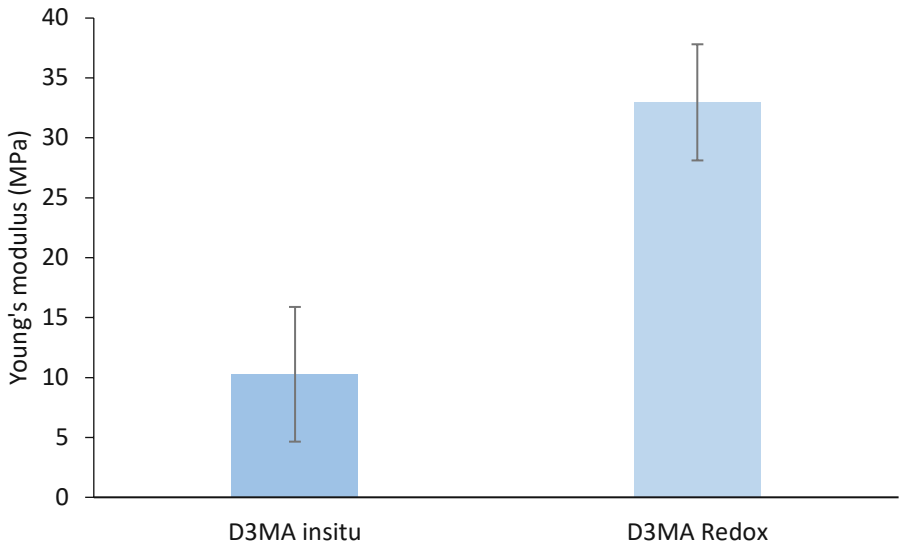

Figure 51: Young's modulus of D3MA in-situ and D3MA Redox

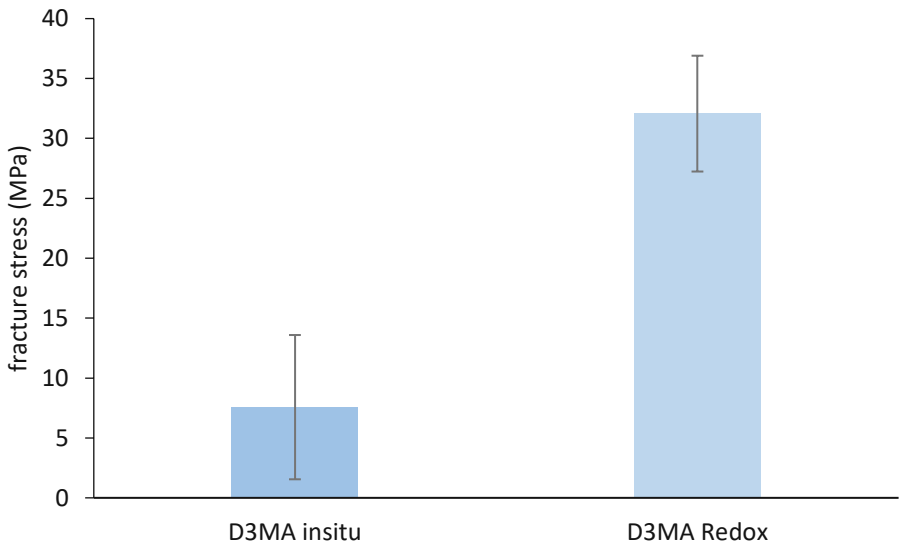

Figure 52: Fracture stress of D3MA in-situ and D3MA Redox

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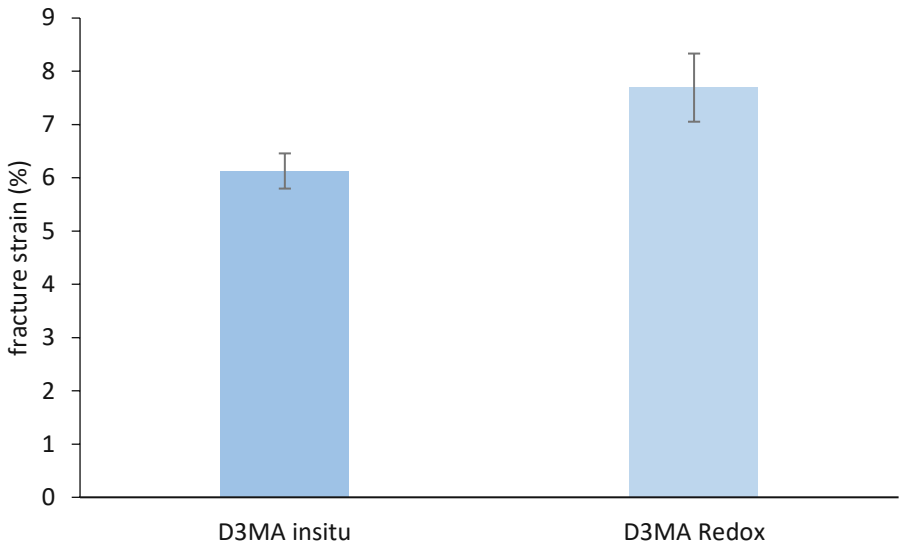

Figure 53:Fracture strain of D3MA in-situ and D3MA Redox

Table 7: Young's modulus, fracture stress and fracture strain of the D3MA in-situ and Redox specimens

	Young's modulus (MPa)	fracture stress (MPa)	fracture strain (%)	DBC (%)
D3MA in-situ	10	8	6.1	85.0
D3MA Redox	33	32	7.7	80.1

The Young's modulus, as well as the fracture stress, are much lower for the in-situ polymerized samples than for the Redox polymerized ones. However, the fracture strain has comparable values to the Redox samples. The overall weaker behavior of the in-situ samples can be explained by the insufficient polymerization in these large sample scales, although the DBC is very similar. The polymerization works very well on a small scale, but it does not seem efficient for larger samples. It can be said that the GTP does not come with the anticipated strengthening of the mechanical properties of the resulting polymers in comparison to free radical polymerization.

2.3.3 Density measurements

In order to evaluate the density change after the polymerization to be able to estimate the volume shrinkage of the polymer, density measurements were conducted. Therefore, the unpolymerized formulation was weighed out in a pycnometer to calculate the density. Afterward, polymerized samples were weighed out with a balance, and the density of the samples was calculated via Archimedes' principle.

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Equation 1: Archimedes' principle for density measurements

$$\rho = \frac{m_{sample} * \rho_{water}}{0.99983 * m_{uplift} *} + 0.0012$$

ρ	density of the sample
m_{sample}	mass of the sample on air
ρ_{water}	density of water at 24 °C (0.99732 g/mL)
0.99983	uplift of the measuring system
m_{uplift}	uplift of the sample in water
0.0012	uplift of the sample on air

The resulting densities of the polymers and monomer mixtures are depicted in Table 8 below.

Table 8: Density of D3MA and the D3MA polymers

	density (g/mL)	shrinkage (%)	DBC (%)
pD3MA in-situ	0.997	4.6	85.0
pD3MA Redox	1.069	12.1	80.1
D3MA	0.953		

As displayed above, the density increases after polymerization. However, the in-situ polymerized sample has a significantly lesser increase of density than the radically polymerized sample. The reason for that is the lesser shrinkage when polymerizing with the controlled in-situ method compared to the free radical polymerization. This concludes in a proof of concept that the controlled behavior of the polymerization has a positive impact on the shrinkage during the polymerization while having a DBC similar to the free radical polymerized samples.

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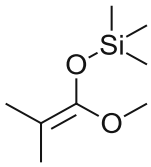
3 Photoinitiated GTP

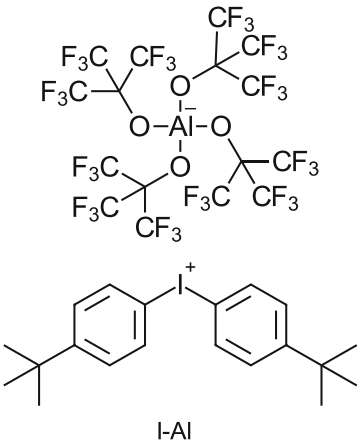
In this thesis, two major initiating methods will be discussed. Second of which is the photoinitiated Group Transfer Polymerization. In this case, a UV-light source will be used to initiate the polymerization. This is an entirely novel technique to initiate group transfer polymerization. In addition, polymerization will not be conducted in a solvent but in bulk. Therefore, formulations were prepared containing monomers, initiator, and a UV-active catalyst. This leaves room for many variables. That is why only one initiator was used in the thesis, namely MTS, which is the most common initiator for GTP (Figure 54).



MTS

Figure 54: 1- Methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS)

As the UV-active catalyst, a phenyliodonium aluminate, that is reported to catalyze photoinitiated cationic polymerization was employed (Figure 55).[46, 47] It is assumed to cleave upon irradiating with UV light and activating the MTS, which then initiates the polymerization.



I-Al

Figure 55: Phenyliodonium aluminate catalyst

In the first chapters of the thesis, the fundamental behavior of the photoinitiated GTP shall be investigated. Therefore, a monofunctional methacrylic monomer was used, namely butylmethacrlyate

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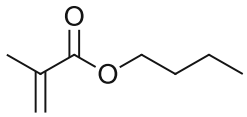
(BMA). The use of the monofunctional monomer enables further analysis for the obtained polymers, such as NMR and GPC, because linear instead of crosslinked polymers are formed.



BMA

Figure 56: Monofunctional butylmethacrylate was chosen as reference monomer

3.1 Linear Polymers

It was assumed that the initiator, MTS, together with a photoacid generator, I-Al, would produce polymers via photoinitiated group transfer polymerization.[46, 48] In the following experiments, the photopolymerization of BMA with MTS and I-Al was investigated in detail via Photo-DSC and subsequent GPC and NMR measurements. All formulations were mixed inside a glovebox and then transferred to the Photo-DSC device under inert conditions. Generally, the formulations were prepared by adding the monomer to a vial and then dissolving the UV-active catalyst. Then the initiator (MTS) was added and fully dissolved. These procedures were always carried out under the exclusion of UV irradiation by working in an orange lab. Subsequent Photo-DSC experiments were always carried out under the same conditions to ensure reproducibility.

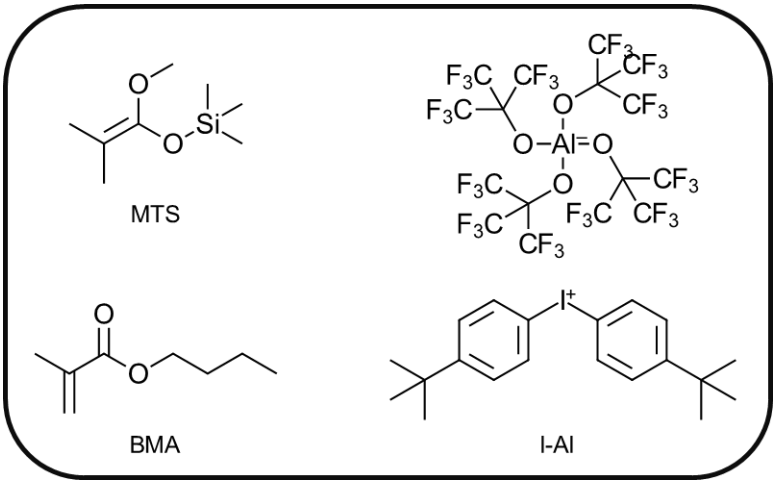


Figure 57: Components of the formulation for Photo-DSC studies with BMA

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3.1.1 Studies with MTS and I-Al

In the first experiments, a formulation containing BMA with 10mol% MTS and 2.5mol% I-Al was prepared inside a glovebox and was a starting point for investigating this system with the aim of a first impression of the photochemical reactivity of this kind of polymerization. The DSC crucibles were weighed out inside a glovebox. In Figure 58 and Table 9 the results of the Photo-DSC measurements are depicted.

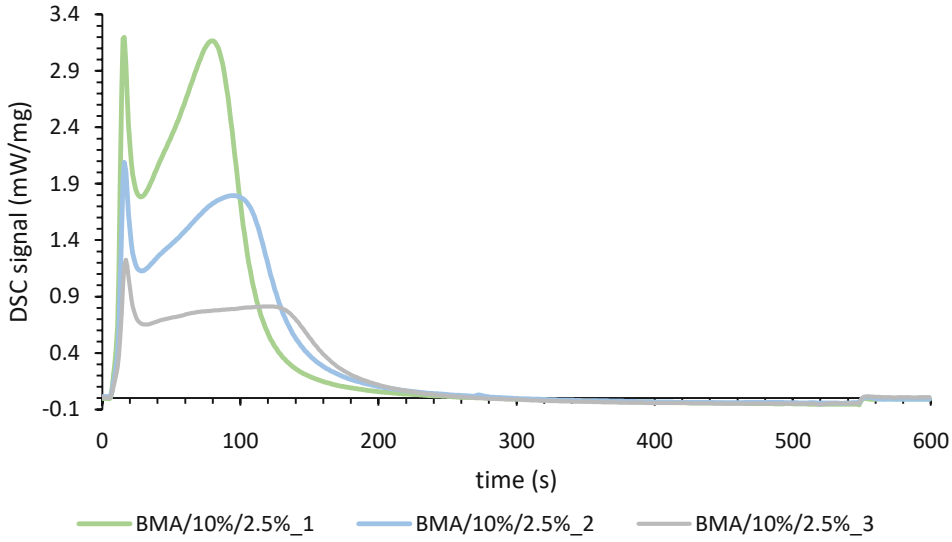

Figure 58: Photo DSC measurement of BMA/10/2.5%

Table 9: Photo-DSC results of BMA/10%/2.5%

	(1)	(2)	(3)
Onset (s)	10.8	11.2	10.9
$Peak_{max}$ (s)	16	16	167
Height (mW/mg)	3.3	2.1	1.3
t_{95} (s)	182	397	214
Area (J/g)	278	216	137

The green curve was the first to measure, blue second and grey third. It is easily visible that the curves' area decreases from (1) to (3), which might be due to the polymerization happening even without the light trigger in advance and may be explained by the high initiator and catalyst content inside the formulation.

Also, the DSC curves show two peaks. The first peak is relatively narrow, and the second peak is slowly increasing and much wider. The grey curve even shows a peak and then more a plateau rather than a

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second peak. It is possible that at first photo-induced radical polymerization is happening before the GTP starts to dominate. GPC and NMR of the samples were measured and are shown below.

Table 10: GPC results of BMA/10%/2.5%

M_n (Da)	3040
PDI ()	1.2
DBC_{DSC} (%)	71
DBC_{NMR} (%)	95

The GPC of the first sample (Figure 58, green) shows one prominent peak at 3040 Da with a PDI of 1.2. The low PDI of the resulting polymer strongly indicates that the BMA was polymerized by GTP rather than free radical polymerization. In addition, the second sample (Figure 58, blue) was quenched with $CDCl_3$ with a drop of methanol right after the measurement and ^{1}H-NMR was measured. The double bond conversion, calculated from the NMR was 95%. The DBC was determined from the Photo-DSC measurement as well since the heat of the polymerization is proportional to the number of double bonds that are polymerizing. The literature value for the polymerization heat per mol double bonds for methacrylates is 56 kJ·mol^{-1} and gives a calculated DBC from the DSC measurement of 71%.[49, 50]

The theoretical heat of the observed polymerization (ΔH_0) was determined from the heat of the polymerization ($\Delta H_{Polymerization}$) and the DBC_{NMR} according to Equation 2.

Equation 2: Calculation of the heat of polymerization

$$\Delta H_0 = \frac{\Delta H_{Polymerization}}{DBC_{NMR}}$$

The ΔH_0 for the depicted measurement is 32 kJ·mol^{-1}, which differs significantly from the literature value of 56 kJ·mol^{-1}.[51] However, this difference may be caused by a polymerization that happens in advance of the irradiation, which would explain the high DBC in NMR despite the low polymerization heat. This would explain the fact that they exhibit a decreasing trend over time.

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3.1.2 Reproducibility

In the previous chapter, the Photo-DSC measurements showed that the samples differ in their reactivity in the DSC when they are all transferred from the glovebox to the Photo-DSC device simultaneously. Having that in mind, the reproducibility of the respective measurements was evaluated. Therefore, samples were prepared with BMA, 10mol% MTS, and 2.5mol% I-Al inside a glovebox and transferred to the Photo-DSC device just before the measurement. The reason for that was to reduce the time before the measurement. The resulting curves are depicted in Figure 59 below.

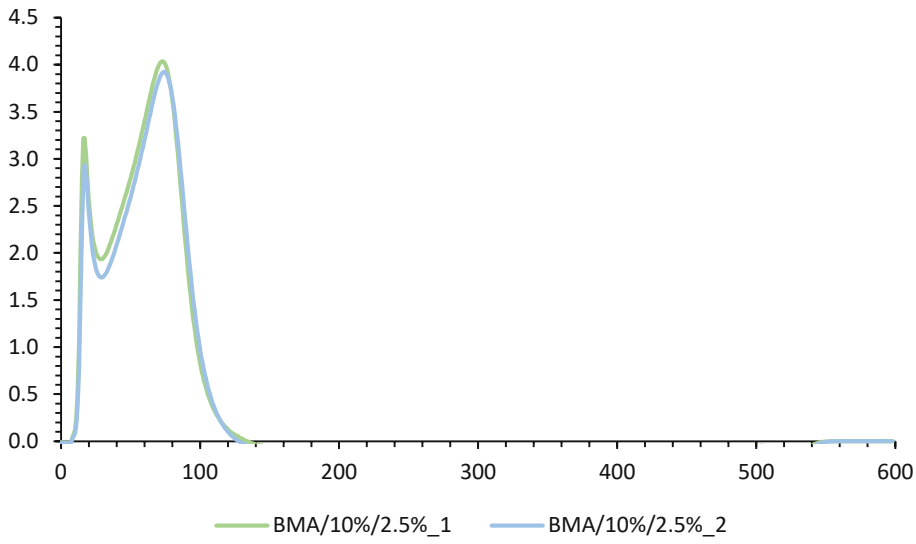

Figure 59: Reproducibility experiment with a formulation containing BMA, 10mol% MTS and 2.5mol% I-Al

Table 11: Results of the reproducibility experiment with a formulation containing BMA, 10mol% MTS and 2.5mol% I-Al

	BMA/10%/2.5%_1	**BMA/10%/2.5%_2**
Onset (s)	11.9	12.1
Peak (s)	73	74
Height (mW/mg)	4.1	4.0
t_{95} (s)	89	90
Area (J/g)	240	228

The form of the peaks is very similar to the peak of the first measurement depicted in Figure 58, which is already a good sign for the reproducibility of the measurements. In addition, the two displayed curves in Figure 59 are almost congruent, and when looking at Table 11, the results are matching as well. All parameters that were measured in the Photo-DSC are very reproducible for both

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measurements. In addition, GPC and NMR were measured as well, which confirmed a low PDI of 1.19 and molecular weights of around 3 kDa with a double bond conversion of 95%.

Table 12: GPC and NMR results of the reproducibility experiment with BMA/10%/2.5%

M_n (Da)	3170
PDI	1.19
DBC_{NMR}	95

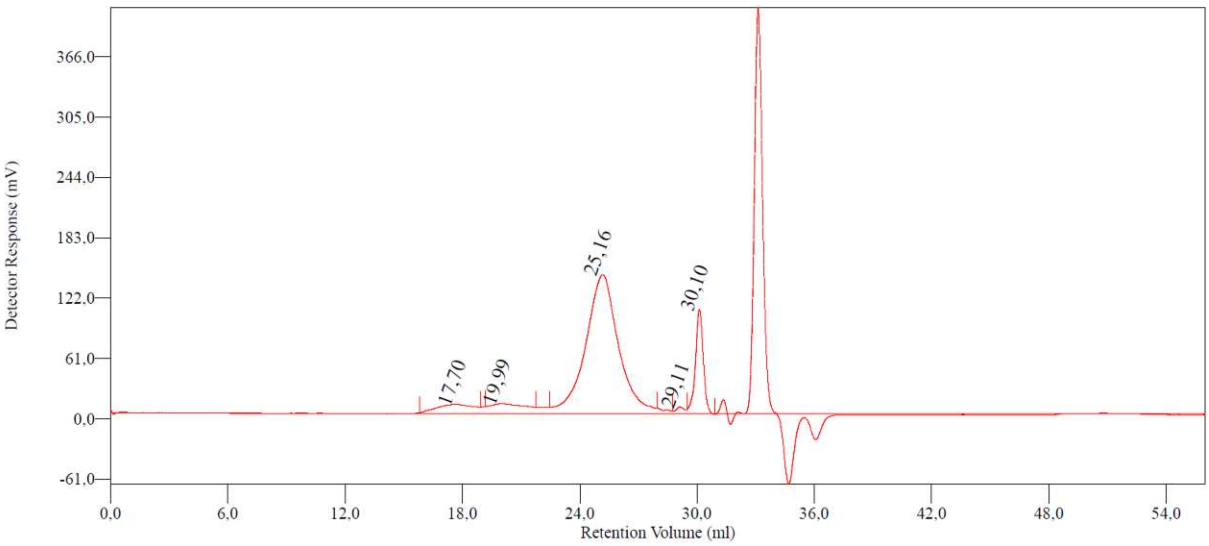

Figure 60: GPC measurement of BMA/10%/2.5%

It is noteworthy that the molecular weight of the main peak at 25.16 mL in the GPC (Figure 60) is double of what would be expected with an initiator to monomer ratio of 1:10. The controlled polymerization should yield polymers of about 1.5 kDa with the used initiator to monomer ratio. This leads to the assumption that two molecules of initiator are consumed for the polymerization of one chain. When looking at the mechanism using trityl salts, the trityl cation abstracts an H-atom of the MTS initiator, which reacts with another MTS molecule to form the initiating species (Figure 61).[31] This mechanism is very suitable for the observed molecular weights and is worth considering here.

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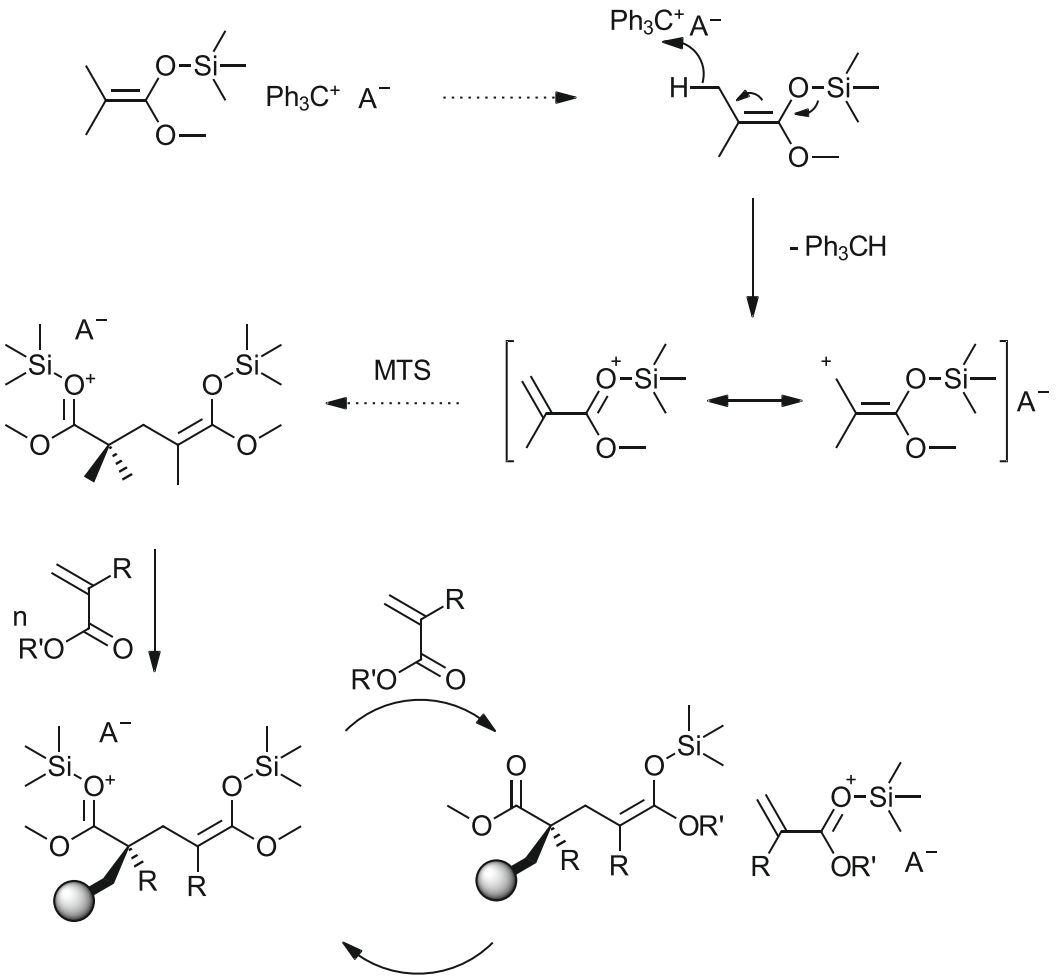

Figure 61: Mechanism of the GTP using trityl salts with MTS and methacrylic monomers[27]

In the shown mechanism, two MTS molecules form a dimeric species through the activation via H-abstraction. The dimer can then repetitively react with the incoming monomer with a transfer of the silyl group to the incoming monomer activating it. This mechanism consumes two molecules of MTS per growing chain, which doubles the expected molecular weight with complete conversion. In the case of the I-Al catalyst, there is no trityl cation; however, upon irradiation, the iodonium cation cleaves in a heterolytic and homolytic fashion, which leads to cationic species, which can abstract hydrogen (Figure 62).

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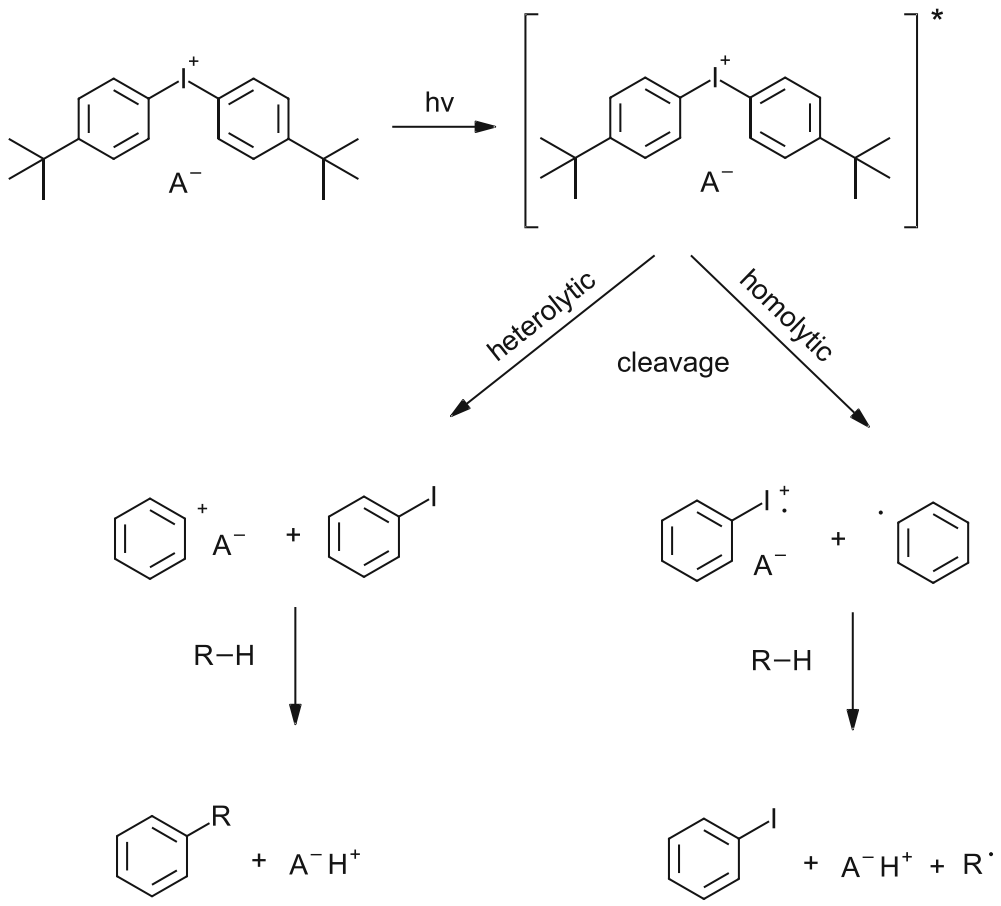

Figure 62: Example of the mechanism of the cleavage of a diphenyliodoniumsalt with an anion (A^-)[47]

In the cleaving mechanism, radical species are generated, potentially initiating a radical polymerization, which could explain the two peaks in the Photo-DSC measurements. Also, the GPC analysis depicted in Figure 60 shows small amounts of polymer at molecular weights of 40-300 kDa, which are explainable with an occurring radical initiation before the GTP takes over.

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3.1.3 Studies without MTS / without I-Al

Since it is reported that MTS can initiate the GTP even without a catalyst when using a suitable solvent, and the I-Al catalyst can initiate radical polymerization, experiments with only MTS and only I-Al in the formulations were conducted.[31] Therefore, formulations with BMA, 10mol% MTS and 2.5mol% I-Al were prepared and either MTS, I-Al or both were left out. To see the effect of the missing parts of the initiating system, Photo-DSC measurements were conducted. The measurements are displayed in Figure 63 in comparison to the respective formulation with MTS and I-Al.

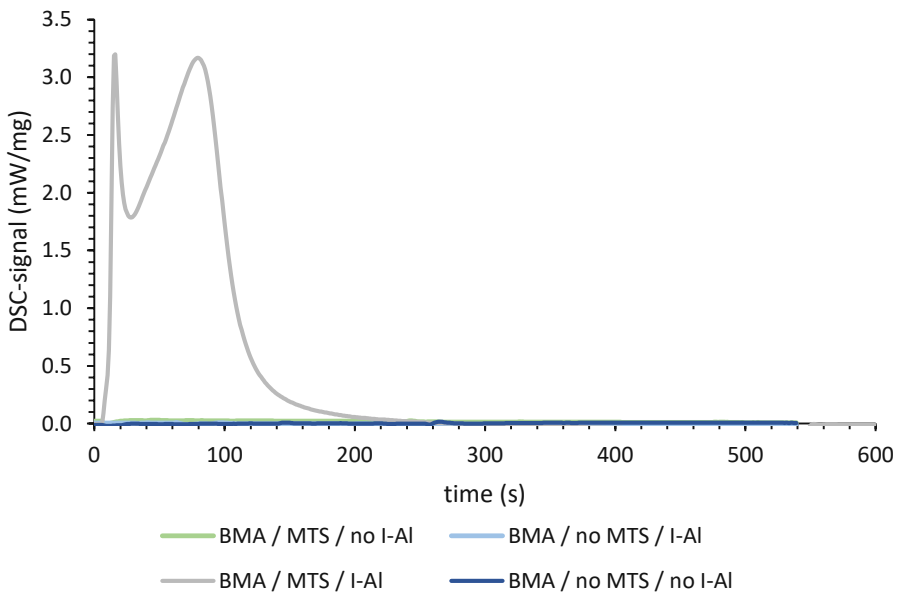

Figure 63: Comparison of formulations, in which either MTS or I-Al is left out

Figure 63 clearly shows that I-Al alone cannot initiate a polymerization on its own, so the radical polymerization observed in the first peak does only occur in the presence of MTS. Also, the formulation with only MTS did not show polymerization. Both components of the initiating system, MTS and I-Al, are necessary for polymerization. The DSC curves of the formulations where either MTS or I-Al are left out show no polymerization reaction. NMR and GPC analysis of the unreactive samples did confirm that no polymerization occurred.

3.1.4 Radical inhibitors

Since the mechanism of the photoinitiated polymerization of BMA with I-Al was considered to be similar to the trityl mechanism, the concentrations were adapted to have a proportion of 2:1 MTS:I-Al

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with 10mol% MTS and 5mol% I-Al to fit the theory, that per I-Al molecule two MTS molecules are consumed. Because there was evidence that radical polymerization occurs in addition to the GTP in the 10% MTS measurements of BMA, formulations with radical inhibitor MEHQ and BHT were investigated. Therefore, formulations were prepared containing BMA with 10mol% MTS, 5mol% I-Al, and 5mol% MEHQ or 5mol% BHT. The formulations were all mixed inside a glovebox and transferred to the Photo-DSC device under inert conditions.

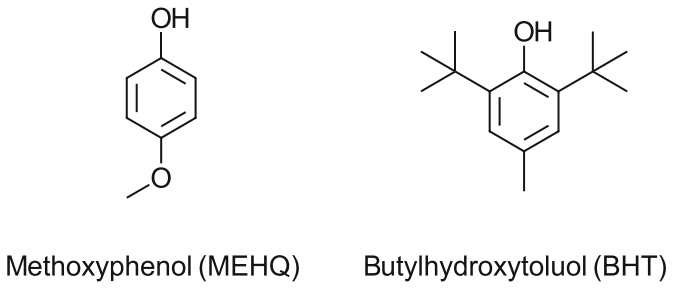

Figure 64: Structure of the radical inhibitors MEHQ and BHT

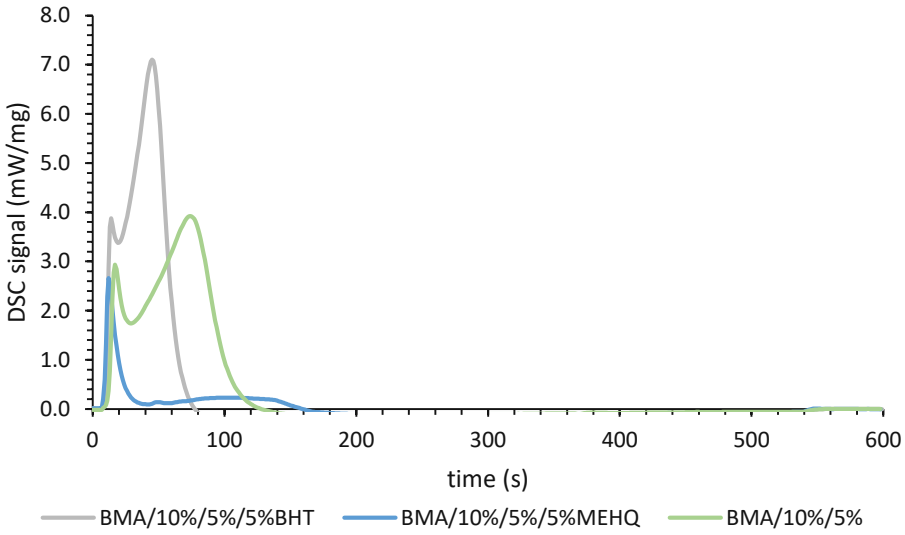

Figure 65: Photo-DSC measurements of BMA/10%/5% with either 5mol% MEHQ or 5mol% BHT

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Table 13: Results of the Photo-DSC measurements of BMA/10%/5% formulation with MEHQ, BHT and without radical inhibitor

	BMA/10%/5%/5%BHT	BMA/10%/5%/5%MEHQ	BMA/10%/5%
Onset (s)	9.7	8.7	12.1
$Peak_{max}$ (s)	48	12	74
Height (mW/mg)	7.1	2.7	4.0
t_{95} (s)	64	82	90
Area (J/g)	262	49	228

This experiment did show fascinating results, which were not expected. Concerning the measurement containing MEHQ, the first peak stays approximately at the same height as in the experiments without MEHQ, but the second peak visible in the previous experiments without MEHQ has almost completely vanished. This is an interesting result, as the first peak was expected to be reduced. A reason might be the unhindered OH-group in MEHQ inhibiting the GTP via proton donation. The GPC analysis showed polymer with molecular weights of 6 kDa and a PDI of 1.77, which do not match with a successful GTP.

However, the experiments with BHT as a radical inhibitor were very promising. It is clearly visible that the formulation containing BHT polymerizes in half the time. Also, the peak is double the height. Very noticeable, however, is that the alleged radical peak has almost disappeared relative to the second peak with 5% BHT in the formulation because it is overlapping with the second peak. For that reason, peak deconvolution was performed of the obtained curve, which is depicted in Figure 66 below.

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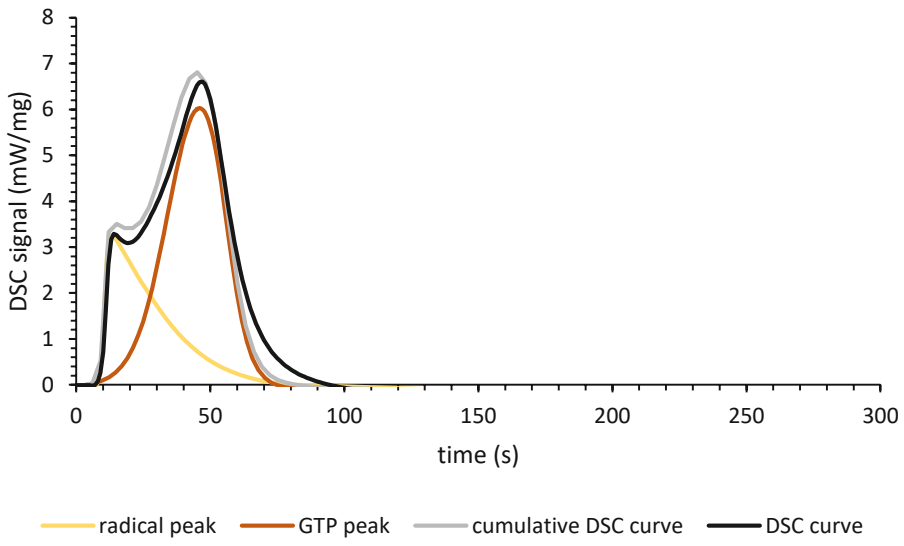

Figure 66: Peak deconvolution of the formulation containing BHT as a radical inhibitor

The peak deconvolution was performed with an asymmetric curve function. The black curve is the original DSC curve, while the grey curve is the sum of the deconvoluted peaks. The areas of the deconvoluted curves are depicted in Table 14 below.

Table 14: Areas of the deconvoluted curve from the Photo-DSC measurement of BMA formulation with BHT as an inhibitor

	Area (J/g)
Peak 1	84.8
Peak 2	169.9

These results show that the first peak contributes to about a third of the curve's total area, and the GTP peak, which is the second peak, adds the majority of the total area. However, the curve of the formulation without BHT was deconvoluted as well, depicted in Figure 67 and Table 15.

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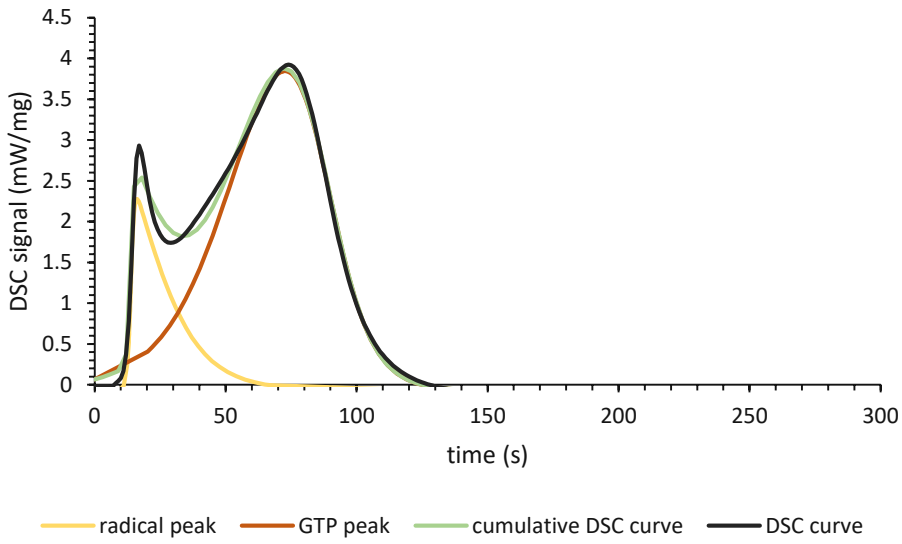

Figure 67: Peak deconvolution of the formulation without inhibitor

The peak deconvolution was performed with an asymmetric curve function. The black curve is the original DSC curve, while the green curve is the sum of the deconvoluted peaks. The areas of the deconvoluted curves are depicted in Table 14 below.

Table 15: Areas of the deconvoluted curve from the Photo-DSC measurement of BMA formulation without inhibitor

	Area (J/g)
Peak 1	43.3
Peak 2	203.4

The area of the first peak in the measurement of the formulation without BHT only contributes to about a fifth of the total peak area. This result is highly interesting since the formulation containing BHT showed overall higher reactivity because it polymerized faster and showed a higher total area. However, the peak deconvolution showed that without a radical inhibitor, the contribution of GTP to the total polymerization heat is higher than with an inhibitor.

Table 16: GPC results of the BMA formulation with and without BHT

	BMA/10%/5%/no inhibitor	**BMA/10%/5%/5%BHT**
M_n (Da)	3170	7360
PDI	1.19	1.96
DBC (%)	100	100

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The higher contribution of radical polymerization of the sample containing BHT is also visible in the molecular weights and the PDI. The sample without inhibitor shows a low PDI of 1.19 with an expected molecular weight of about 3 kDa. The sample with inhibitor has a much broader molecular weight distribution and also higher molecular weights.

3.1.5 Storage stability

Storage stability for photopolymerizable formulations is an essential factor when handling the formulations in their applications. Therefore, BMA was tested for its storage stability with 1mol% and 10%mol MTS and different concentrations of the I-Al catalyst. The formulations were stored at room temperature under exclusion of UV light and the time from mixing the polymerization until gelation of the formulation was measured, and the results are depicted in Table 17.

Table 17: Storage stability of formulations with I-Al and 1mol% and 10mol% MTS

	1mol% MTS	**10mol% MTS**
BMA 0,1mol% I-Al	n.p.*	n.p.*
BMA 5mol% I-Al	n.p.*	< 1 day

* no polymerization after two weeks

As shown in the table above, the storage stability of the formulations is not very good, except for the formulations containing 1mol% MTS and 0,1mol% I-Al, which is stable for at least two weeks.

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3.2 Networks

In mind of the application in dental materials, not only monofunctional systems were investigated, but also difunctional monomers forming networks. Therefore, common monomers used in dental fillings were investigated regarding their reactivity in GTP systems. To get an overview, a screening was conducted. The used catalysts and monomers are depicted in Figure 68 and Figure 69.

3.2.1 Screening of catalysts

In order to get an overview of the various catalysts that could be used in photoinitiated GTP, a screening of literature known catalysts with the different monomer mixtures was performed. The iodonium aluminate (I-Al) is an already used photoinitiator for cationic polymerization of, e.g., epoxides, that initiates by releasing a superacid.[46, 48] This is very feasible for GTP since it can be initiated with acids.

Trityl tetrakis(pentafluorophenyl)borate is a literature-known catalyst for GTP that is mainly used for 2K systems. However, photoreactivity was assumed, which lead to the inclusion of the catalyst.[27, 31] As initiator MTS was used since it is the most common initiating species for the GTP and already showed high reactivity in the monofunctional systems (3.1).

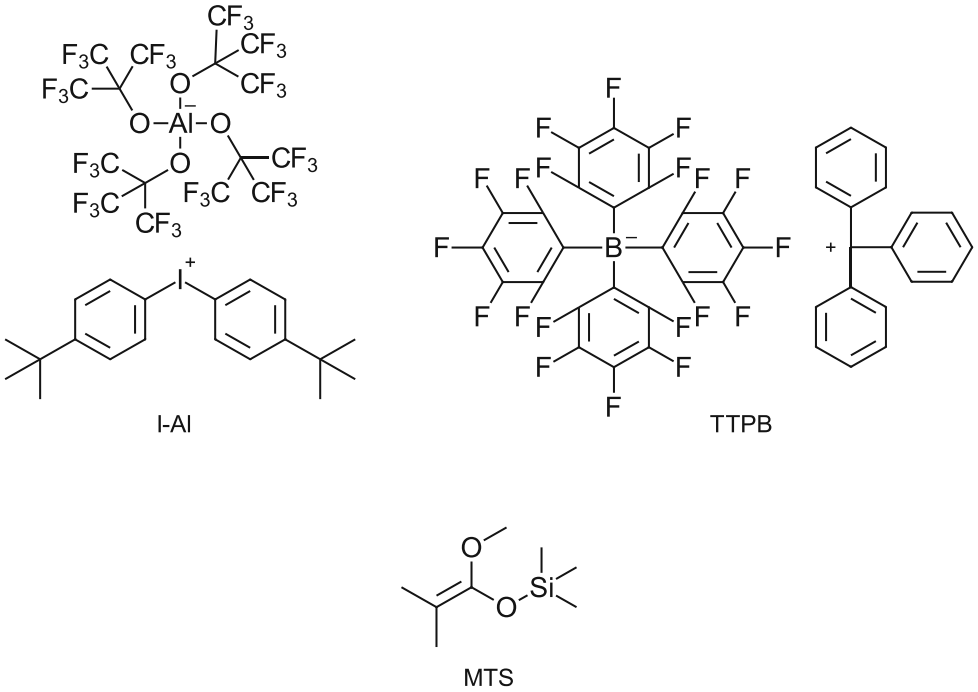

Figure 68: Initiator MTS and catalysts used for the screening with difunctional monomers

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The monomer mixture that was chosen for these experiments was based on the experiences with monomers in the 2K systems (2.2). Therefore, monomers without any protic groups were selected, which led to the choice of V-224 as a derivative of BisGMA without the hydroxy group and TEGDMA, as it is a common monomer used in dental materials. These monomers were kindly provided by Ivoclar AG in a 70wt%:30wt% V-224:TEGDMA mixture (MIX1).

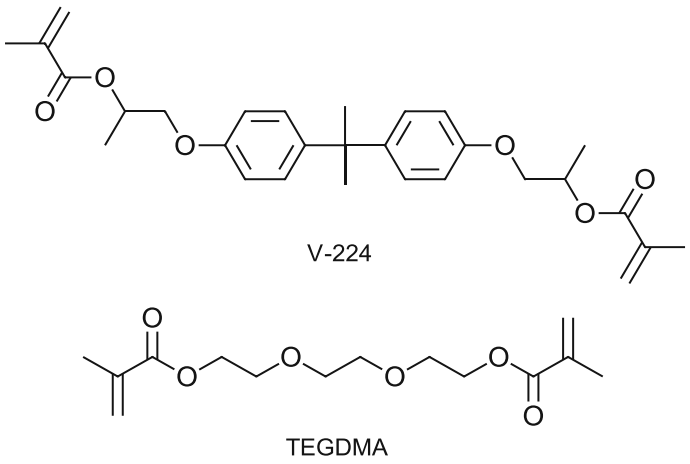

Figure 69: Difunctional monomers used for the photoinitiated GTP (MIX1)

For the Photo-DSC measurements, the formulations containing MIX1, 10mol% MTS, and 5mol% I-Al or TTPB, respectively, were prepared and weighed out inside a glovebox under the exclusion of UV-light. The samples were then transferred carefully to the Photo-DSC device, where they were measured immediately. However, the samples containing TTPB as a catalyst formed a skin on the top of the formulation when all components were mixed. The residual liquid under the skin was still measured, and the results are depicted in Figure 70 and Table 18.

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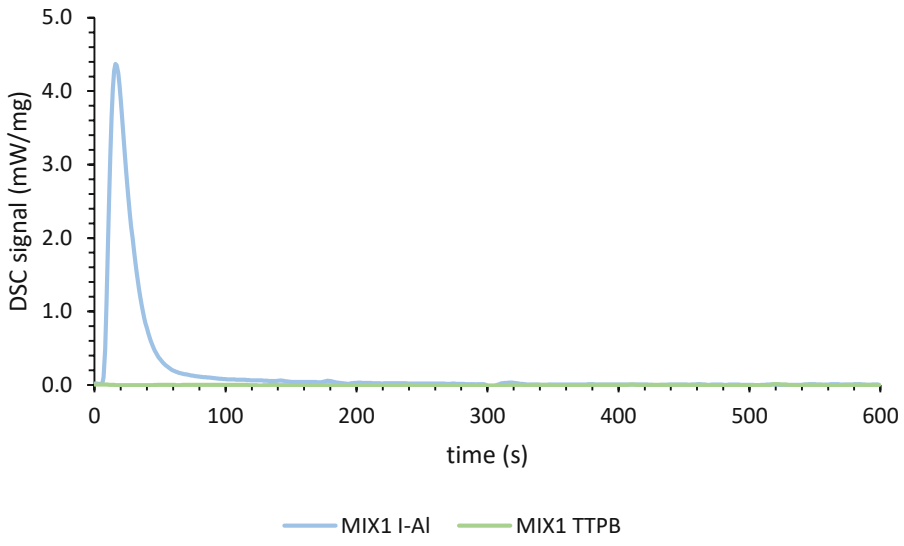

Figure 70: Photo-DSC measurement of MIX1 with 10mol% MTS and 5mol% I-Al or TTPB

Table 18: Photo-DSC results of MIX1 with 10mol% MTS and 5mol% I-Al

	MIX1/10% MTS/5% I-Al
Onset (s)	7.5
$Peak_{max}$ (s)	16.3
Height (mW/mg)	4.4
t_{95} (s)	129
Area (J/g)	99.5

The aluminate catalyst, I-Al, does show a significant reactivity with the MIX1 monomers. Especially the Onset and the time of the peak maximum is very low. Overall, polymerization occurs very fast. In contrast, the borate catalyst, TTPB, does not show any polymerization in the Photo-DSC. This is very likely due to the formation of the polymer skin upon mixing, which reduces the number of initiating molecules drastically.

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3.2.2 UV-Vis measurements

The I-Al catalyst was performing very well in the first tests with the MIX1 monomers and MTS, which is why UV-Vis measurements were performed to find out the absorption behavior. Also, the borate catalyst, as well as MTS, were being measured to see if they obtain any absorption qualities. Solutions of 0.001 mol/L in acetonitrile of the TTPB catalyst and 0.005 mol/L of the I-Al catalyst were prepared and measured. The resulting spectra are depicted below.

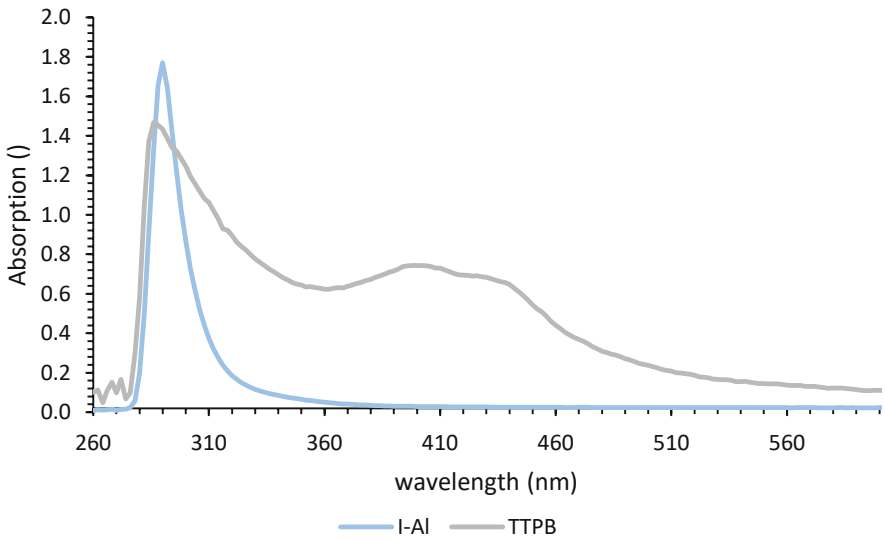

Figure 71: UV-Vis spectrum of 0.001 mol/L TTPB and 0.005 mol/L I-Al in acetonitrile

Figure 71 show that both I-Al and TTPB have absorption maxima below 300 nm. Both have their maximum at 286 nm. However, TTPB has a second peak at around 400 nm. The absorption in higher wavelengths also correlates to the yellow/brown color of TTPB.

The results of the measurement of the 0,3 mol/L MTS-solution is shown in Figure 72.

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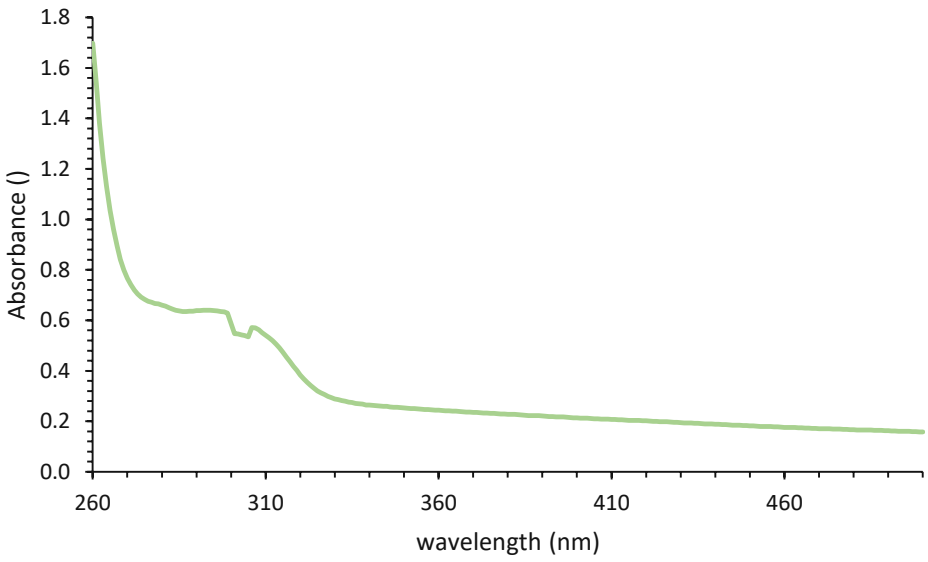

Figure 72: UV-Vis measurement of MTS of a 0,3 mol/L solution in acetonitrile

Figure 72 shows that there is an absorption maximum at 306 nm. Although considering the measured concentration of MTS, the absorption is still very low. The molar extinction coefficient of MTS was calculated with a value of 0,195 $L \cdot mol^{-1} \cdot cm^{-1}$.

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3.2.3 UV activity of trityl salt

Since it was found that the trityl borate catalyst (TTPB) displayed in Figure 73 shows UV-activity and could be suitable for photoinitiated GTP, experiments were performed to understand this system better.

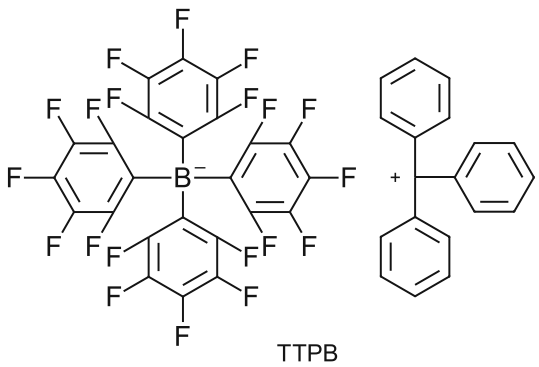

Figure 73: Trityl borate catalyst (TTPB)

An experimental setup was designed depicted in Figure 74 to find out which species is the crucial part for the polymerization of MIX1 with 5mol% TTPB and 10mol% MTS.

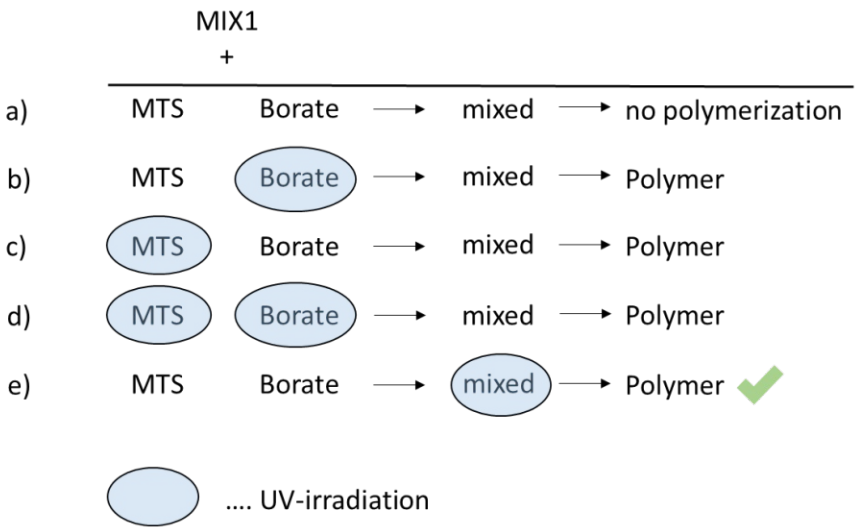

Figure 74: Experimental setup for TTPB experiments

It was already known that the monomer mixture with TTPB and MTS polymerizes (Figure 74 e)). Row a) displays the reference where no irradiation is performed, in which no polymerization should occur in theory. Rows b) - d) show cases in which only one component or both of the initiating system is irradiated separately and mixed afterward. The goal was to see if, e.g., only borate with monomers

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was irradiated and mixed with MTS and monomer afterward, a polymerization would occur and if the activated species that is formed via the irradiation comes from either borate or MTS alone.

Surprisingly, all the formulations depicted in Figure 74 were polymerized after irradiation, which, however, might be due to the heat development inside the UV-oven where the experiment was conducted. Also, the intensity of the UV-oven is set to 120 mW/cm^2, which is more than three times the intensity of the Photo-DSC irradiation, which is set at 35 mW/cm^2. Nevertheless, it can be concluded that borate and MTS form active species upon irradiation that can initiate a polymerization reaction.

3.2.4 Studies without MTS / without I-Al

The borate catalyst TTPB did not show any reactivity in the Photo-DSC, although UV-Vis measurements showed an absorption below 300 nm. Despite this absorbance, it does seem more suitable as a 2K catalyst since polymerization starts immediately after mixing. For these reasons, further investigations were performed only with the I-Al catalyst. To investigate the behavior of this MIX1/MTS/I-Al system a bit deeper, variations of it were prepared, where either MTS, I-Al, or both were absent. These measurements were conducted with MIX1, 10mol% MTS, and 5mol% I-Al. All formulations were prepared and weight out inside a glovebox under the exclusion of light. They were transferred to the Photo-DSC device inert and measured immediately. The resulting Photo-DSC measurements are displayed in Figure 75.

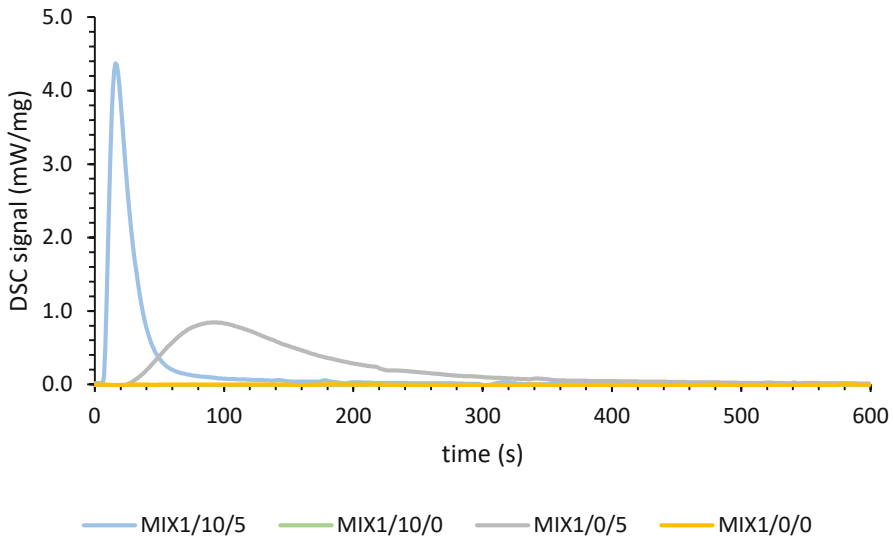

Figure 75: Photo-DSC measurement of MIX1 with 10mol% MTS and 5mol% I-Al (blue)
green: no I-Al was added
grey: no MTS was added
yellow: MIX1 alone

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It is clearly visible that the formulation containing only MIX1 does not polymerize, which was expected. In addition, the formulation containing only MTS did not polymerize as well. However, surprisingly, the formulation containing no MTS, but only I-Al catalyst, did show a polymerization. A reason for this might be a slowly induced radical polymerization that does occur if no GTP is possible in the first place. In chapter 3.1, it was already shown that a radical polymerization could be initiated with the I-Al catalyst. The analysis of both curves is depicted in comparison in Table 19. For calculation of the DBC, a literature value of 56 kJ mol^{-1} was used.[51]

Table 19: Comparison of MIX1 with 10mol% MTS and 5mol% I-Al, with the same formulation but without MTS

	MIX1/10% MTS/5% I-Al	**MIX1/0% MTS/5% I-Al**
Onset (s)	7.5	26.6
$Peak_{max}$ (s)	16.3	92.8
Height (mW/mg)	4.4	0.8
t_{95} (s)	129	291
Area (J/g)	99.5	108.8
DBC_{DSC} (%)	25	28

The onset and the time of the maximum of the peak are much higher than in the curve of the formulation that contains MTS. However, the resulting area is very comparable. It can be concluded that GTP is only possible if all components of the initiating system are within the formulation. However, if only I-Al is present, a slowly induced radical polymerization occurs.

3.2.5 Studies with different MTS / I-Al concentration

To better understand the role of MTS in the polymerization of the MIX1 monomer mixture with I-Al, Photo-DSC measurements were made with different concentrations of MTS. Formulations were prepared containing 1mol%, 2mol%, or 10mol% of MTS initiator. The results are shown in Figure 76 and Table 20.

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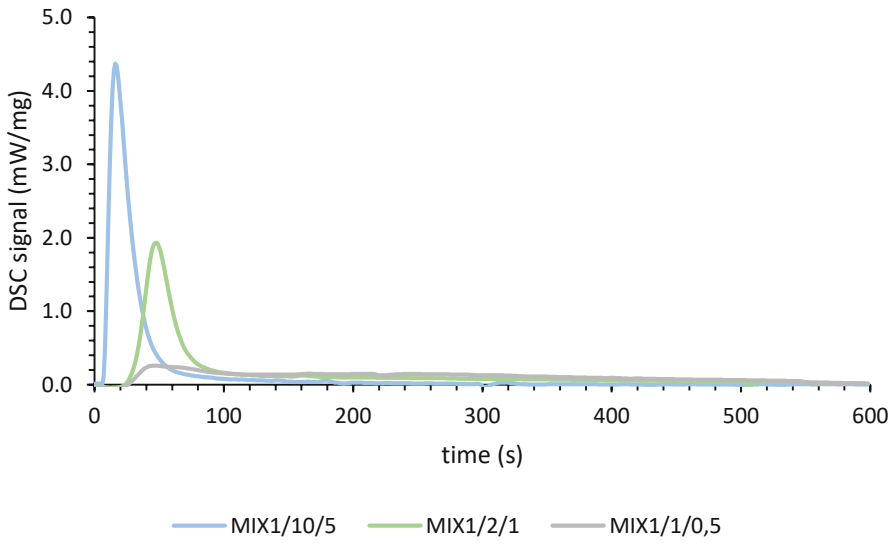

Figure 76:Photo-DSC measurements of MIX1 with MTS and I-Al in different concentrations

Table 20: Photo-DSC results of the measurement of MIX1 with MTS and I-Al in different concentrations

	MIX1/10% MTS/5% I-Al	**MIX1/2% MTS/1% I-Al**
Onset (s)	7.5	30.4
$Peak_{max}$ (s)	16.3	47.4
Height (mW/mg)	4.4	1.9
t_{95} (s)	129	321
Area (J/g)	99.5	69
DBC_{DSC} (%)	25	18

As clearly visible in Figure 76, a higher concentration of MTS in the formulation results in a significant increase of the polymerization activity as the area and height increase and the time to reach the $Peak_{max}$ decreases. As shown in Table 20, the area of 10mol% MTS formulation is a third higher than of the 2mol% MTS formulation. Also, the $Peak_{max}$ is reached in less than a third of the time. This makes a polymerization with a high concentration of 10mol% much more attractive. The formulation with only 1mol% MTS and 0.5mol% I-Al did show only neglectable polymerization and was not evaluated. From this measurement, it is evident that the 10mol% MTS and 5mol% I-Al formulation is the best choice for a successful GTP, and the smaller the amount of initiating species get, the slower and less reactive the polymerization gets.

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3.3 Thermomechanical tests

As discussed in detail in chapter 2.2.2, the protic groups of UDMA or BisGMA are potentially inhibiting the GTP (Figure 77). As a result, monomers without protic groups were selected for mechanical tests (Figure 78).

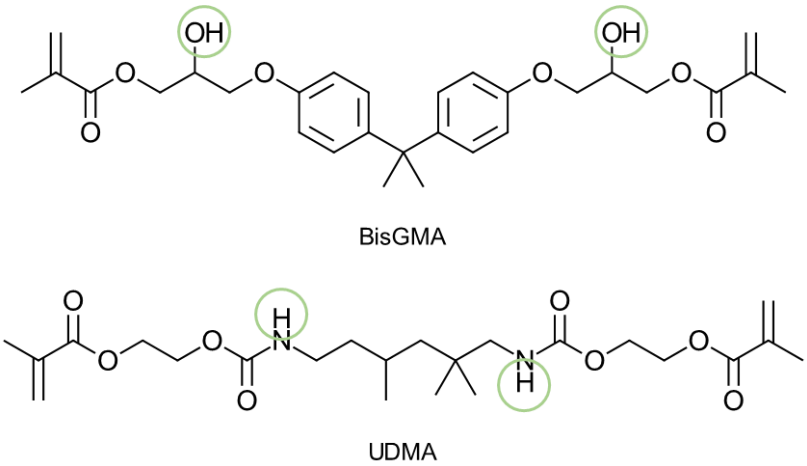

Figure 77: Protic groups of UDMA and BisGMA

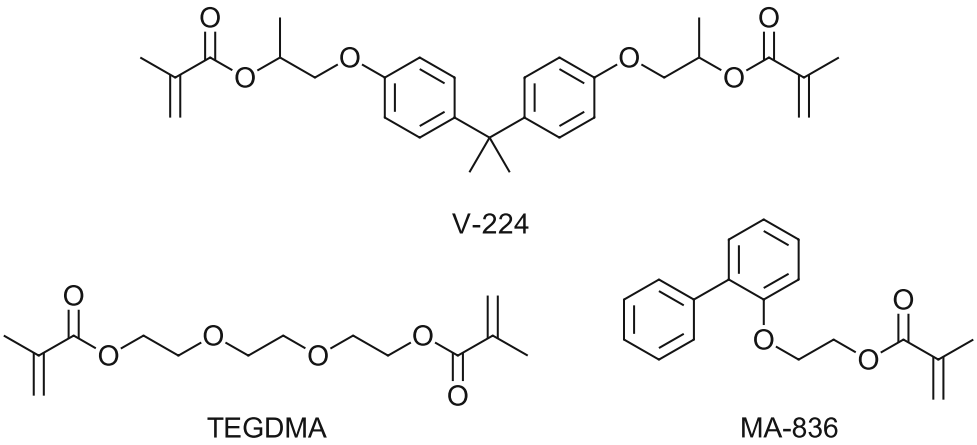

Figure 78: Methacrylate monomers without protic groups

V-224 is a derivative of BisGMA without the OH-group, which makes it an easy choice. TEGDMA is a common dimethacrylate for dental polymers, and MA-836 is a monofunctional methacrylate with a higher viscosity that leads to proper materials. The mixtures of these monomers depicted in Table 21 were kindly provided by Ivoclar AG.

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Table 21: Composition of formulations with non-protic monomers

MIX1		MIX2	
	wt%		wt%
V-224	70	V-224	70
TEGDMA	30	MA-836	30

3.3.1 Photo-DSC

Formulations were prepared of MIX1 and MIX2 with 10mol% MTS, and 5mol% I-Al and Photo-DSC experiments were conducted. MIX2, unfortunately, was too high-viscous to be correctly transferred into the aluminum crucible for the measurement inside the glovebox. However, a comparable reactivity to MIX1 was assumed. As a radical reference, Ivocerin (Figure 79) was chosen and formulations with 0.5wt% Ivocerin were prepared with MIX1 to confirm the reactivity. In Figure 80, the Photo-DSC measurement of MIX1 with the GTP system and the radical reference system using Ivocerin is displayed. In Figure 81, the double bond conversion is shown.

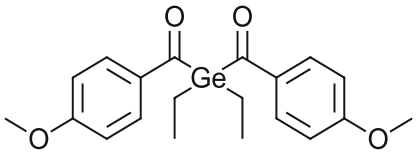

Figure 79: structure of Ivocerin

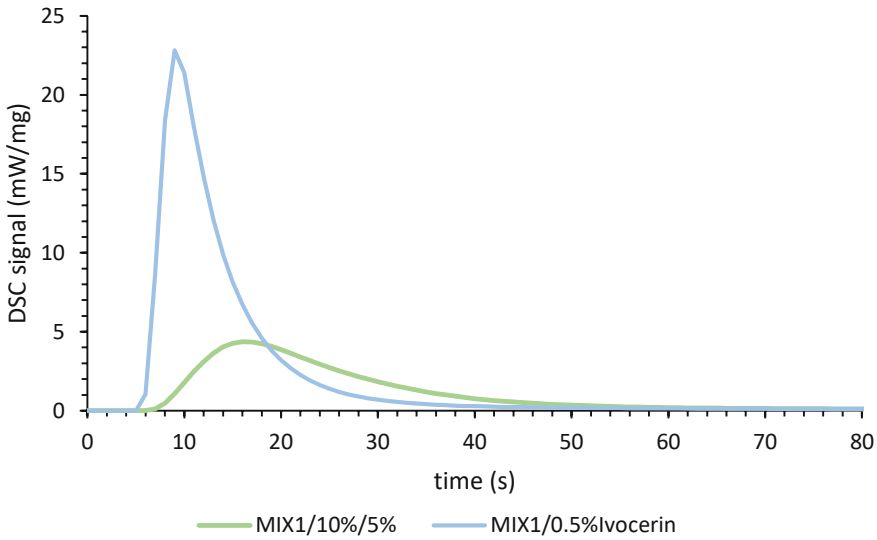

Figure 80: Photo-DSC measurement of MIX1 with the GTP system and with Ivocerin

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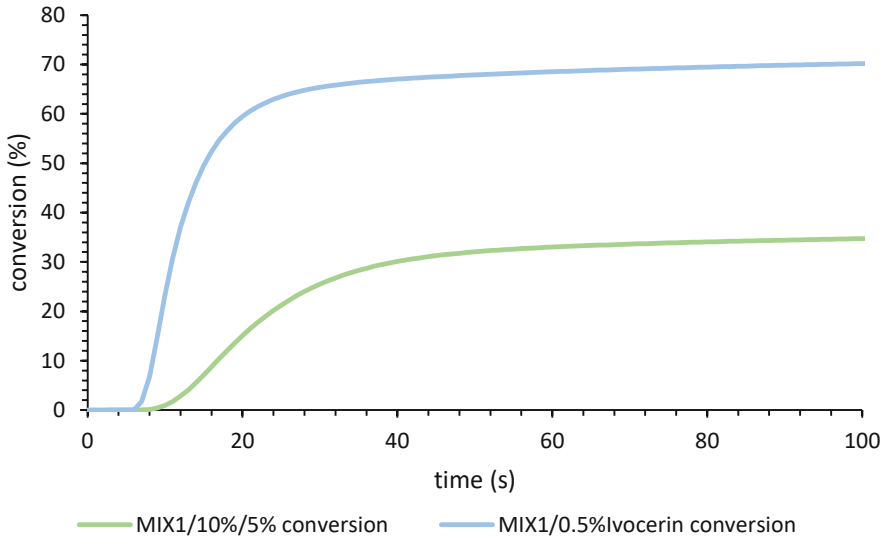

Figure 81: Photo-DSC measurement of MIX1 with Ivocerin as a reference

Table 22: Comparison of MIX1 with Ivocerin and MTS/I-Al

	MIX1/10%/5%	**MIX1/0.5%Ivocerin**
Onset (s)	7.5	6.1
$Peak_{max}$ (s)	16.3	9.2
Height (mW/mg)	4.4	22.9
t_{95} (s)	129	96
Area (J/g)	99.5	195.5
DBC_{DSC} (%)	36.4	73.8

It is clearly visible that Ivocerin shows higher conversions and a faster polymerization, however, $Peak_{max}$ and Onset are very comparable. Hence, it seems that MIX1 with MTS/I-Al, although it does not yield as high conversions as Ivocerin, is a very reactive system and leads to a comparably fast polymerization.

As a consequence of the successful Photo-DSC measurement, it was decided to prepare DMTA specimens to obtain the thermomechanical properties of the polymers.

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3.3.2 DMTA

DMTA specimen were prepared of MIX1 and MIX2. Therefore, MIX1 and MIX2 with 10mol% MTS and 5mol% I-Al were mixed inside the glovebox and transferred into the mold for the DMTA specimen. The mold was inside an airtight box under an argon atmosphere with a quartz-glass window to allow irradiation of the sample. Furthermore, reference specimens with 5mol% Ivocerin as radical initiators were prepared to compare the GTP to free radical polymerization.

The measurements were conducted from -100 °C to 200 °C. In this range, the first measurement (MIX1 I-Al #1) induced a post-curing process in the GTP specimen, leading to repeat the measurement to see if there are differences in the thermomechanical properties (MIX1 I-Al #2). The data of the measurements are depicted in Figure 82 and Figure 83.

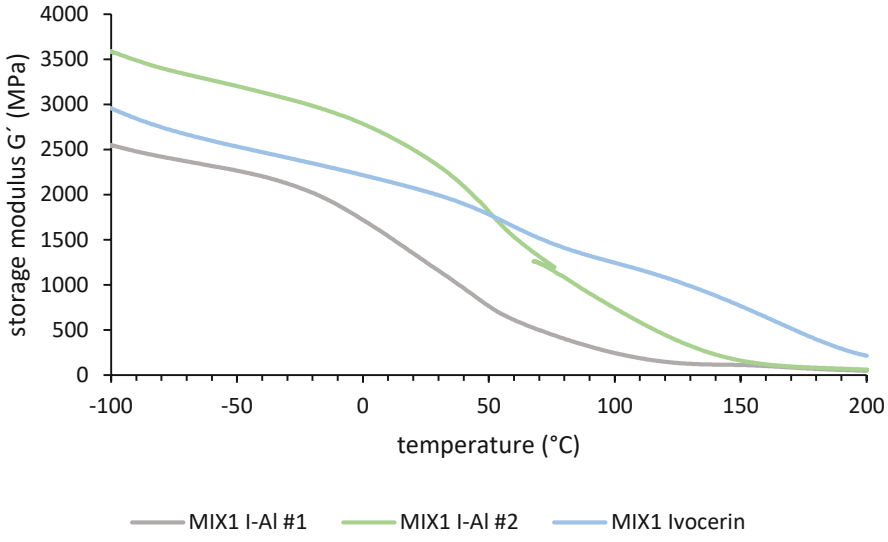

Figure 82: Storage moduli of MIX1 I-Al in both measurements and the Ivocerin reference

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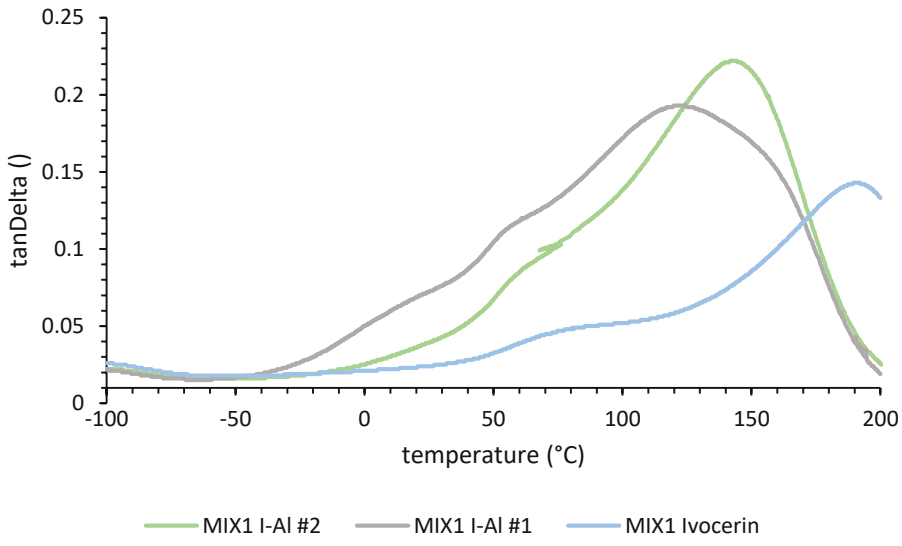

Figure 83: tanδ of MIX1 I-Al in both measurements and the Ivocerin reference

The storage modulus of all specimens at -100 °C is in the same order of magnitude, however, the progression differs, which is also clearly visible in the tanδ values. The peak of the tanδ curve is at the glass transition temperature (T_g). As can be seen in Figure 83, the T_g of both measurements of the GTP polymerized specimen is more than 50 °C lower than the radically polymerized specimen, although the second measurement depicts a higher T_g than the first one, which may be explained by the thermal postcuring during the first measurement. The T_g's are summarized in Table 23. Also noticeable in the measurements is the broad tanδ peak of all the samples, which makes the obtained T_g values a bit unreliable. The full width at half maximum for the first measurement is 65°C and for the second measurement it is 45°C. Especially the difference in the T_g between MIX1 I-Al #1 and MIX1 I-Al #2 may not be exactly, what is measured because the curves in Figure 83 show significant similarities, only that MIX1 I-Al #2 is a bit lower, which causes the T_g to be much lower.

Table 23: T_g's and DBC of the MIX1 specimens

	T_g (°C)	DBC (%)
MIX1 I-Al #1	111	-
MIX1 I-Al #2	143	68.1
MIX1 Ivocerin	190	56.8

The DBC of the specimens was determined via ATR-IR by correlating the integrals of the C=C stretch band at 1640 cm^{-1} before and after the polymerization. Furthermore, even though no Photo-DSC measurements could be conducted with MIX2, DMTA specimen were prepared and measured. The results are depicted in the following Figure 84 and Figure 85.

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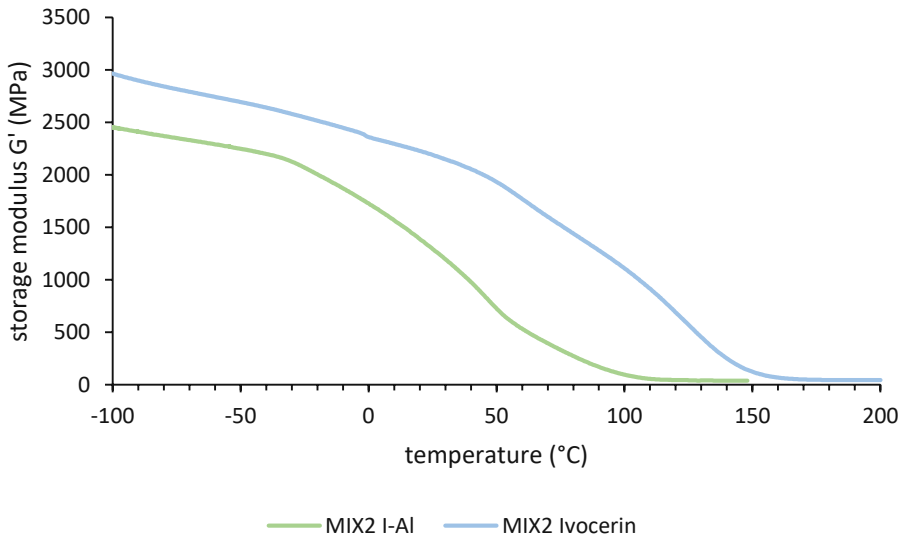

Figure 84: Storage moduli G' of MIX2 with I-Al and Ivocerin

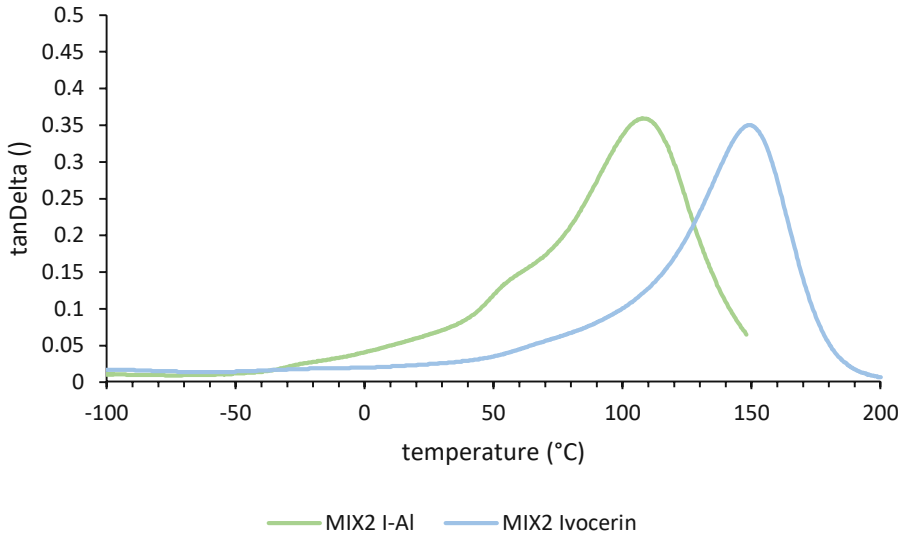

Figure 85: tanδ of MIX2 with I-Al and Ivocerin

Table 24: T_g's and DBC of the MIX2 specimens

	T_g (°C)	DBC (%)
MIX2 I-Al	108	27.6
MIX2 Ivocerin	125	36.9

As depicted above, the specimen with I-Al broke at around 150 °C, but fortunately, the T_g is lower and therefore still clearly visible. For this sample, no second measurement was possible. The same trend as with MIX1 can be seen; the T_g shifts to lower temperatures when using I-Al instead of Ivocerin.

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However, in the MIX2 samples, the peaks seem to be much sharper and the shift to lower temperatures is obvious. The full width at half maximum for the I-Al specimen is 59 °C, which is much higher than the Ivocerin specimen with only 23 °C. The DBC of these specimens also correlates very well with observed T_g values, as lower DBC goes along with a lower T_g.

3.3.3 Tensile tests

Specimen for tensile tests were prepared of MIX1 and MIX2. Therefore, MIX1 and MIX2 with 10mol% MTS and 5mol% I-Al were mixed inside the glovebox and transferred into the mold for the tensile test specimen. The mold was inside an airtight box under an argon atmosphere with a quartz-glass window to allow irradiation of the sample. Furthermore, reference specimens with 5mol% Ivocerin as radical initiators were prepared to compare the GTP to free radical polymerization. The Young's modulus, as well as strain and stress at break are depicted in the diagrams below.

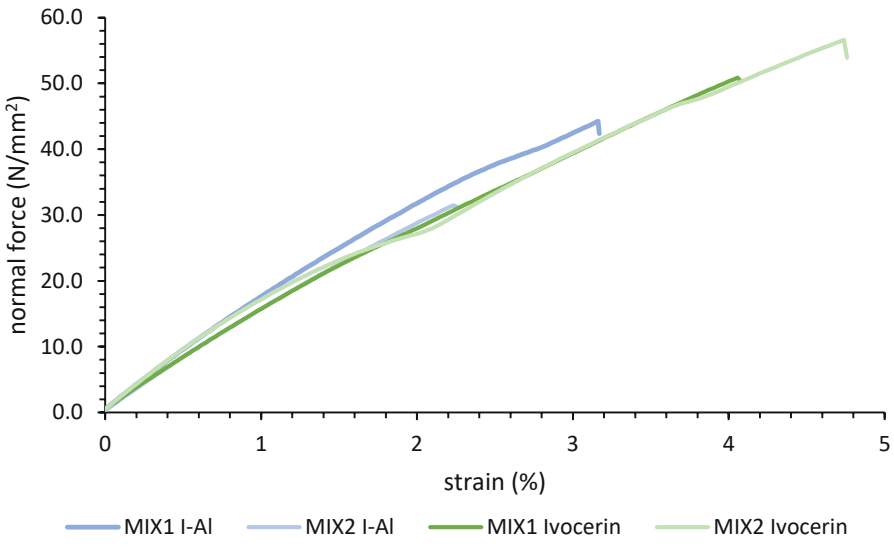

Figure 86: Stress-strain diagram of the tested specimens

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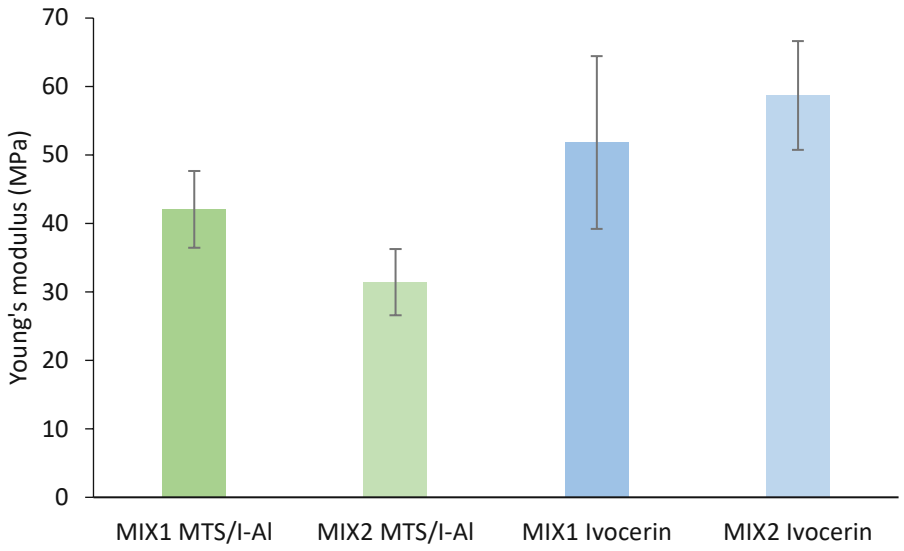

Figure 87: Young's modulus of MIX1 and MIX2 samples polymerized with MTS/I-Al or Ivocerin

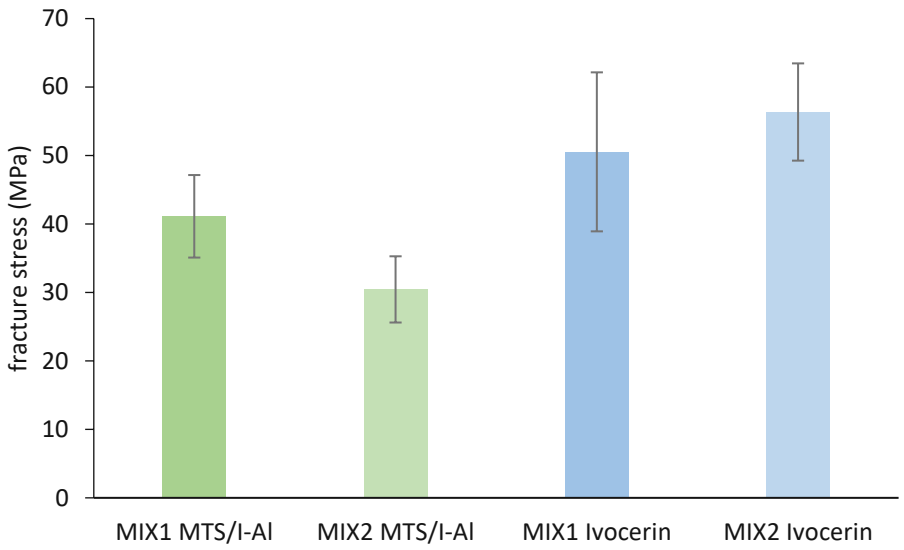

Figure 88: Fracture stress of MIX1 and MIX2 samples polymerized with MTS/I-Al or Ivocerin

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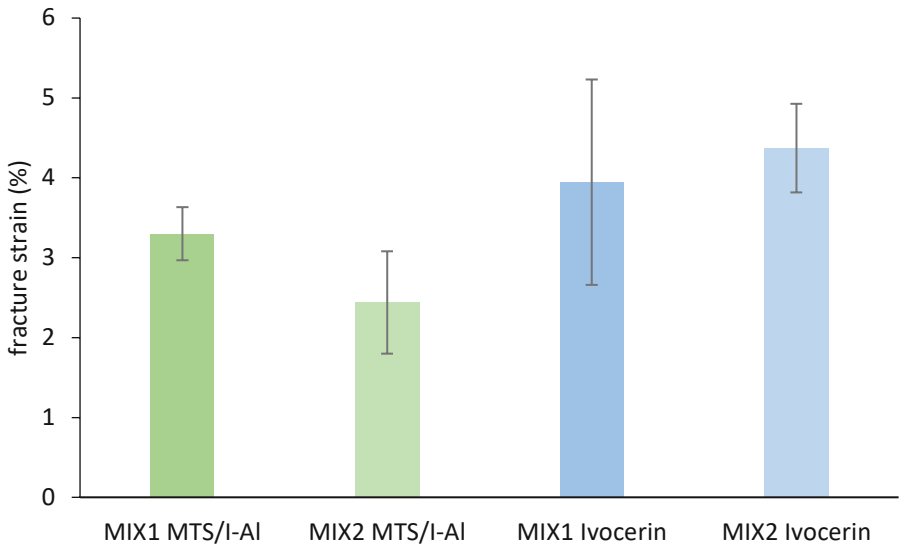

Figure 89: Fracture strain of MIX1 and MIX2 samples polymerized with MTS/I-Al or Ivocerin

Table 25: Results of the tensile tests of MIX1 and MIX2 with MTS/I-Al and Ivocerin

	Young's modulus (MPa)	fracture stress (MPa)	fracture strain (%)	DBC (%)
MIX1 MTS/I-Al	42	41	3.3	68.1
MIX2 MTS/I-Al	31	30	2.4	27.6
MIX1 Ivocerin	52	51	4.0	56.8
MIX2 Ivocerin	59	56	4.4	36.9

The samples that were polymerized via GTP exhibit a clear trend for all the parameters. MIX1 has within the deviation a higher Young's modulus, fracture strain and fracture stress than MIX2. Interestingly, the same trend cannot be observed for the samples that were polymerized with Ivocerin. However, the deviation of the MIX1 Ivocerin sample is relatively high, which may cause the trend to appear inverted. If the two polymerization techniques are compared directly, it is evident that the samples polymerized radically with Ivocerin are performing better. Also, the DBC of the radically polymerized samples is around 10% higher than the GTP polymerized samples. The expected strengthening of the polymer through homogeneous networks cannot be observed in this case.

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3.3.4 Density measurements

To evaluate the density change after the polymerization to be able to estimate the volume shrinkage of the polymer, density measurements were conducted. Therefore, the unpolymerized formulation was weighed out in a pycnometer to calculate the density. Afterward, polymerized samples were weighed out with a balance, and the samples' density was calculated via Archimedes' principle.

Equation 3: Archimedes' principle for density measurements

$$\rho = \frac{m_{sample} * \rho_{water}}{0.99983 * m_{uplift} *} + 0.0012$$

ρ	density of the sample
m_{sample}	mass of the sample on air
ρ_{water}	density of water at 24 °C (0.99732 g/mL)
0.99983	uplift of the measuring system
m_{uplift}	uplift of the sample in water
0.0012	uplift of the sample on air

The resulting densities of the polymers and monomer mixtures are depicted in Table 26 below.

Table 26: Density, shrinkage and DBC of MIX1 and MIX2 as well as the MIX1 and MIX2 polymers

	density (g/mL)	shrinkage (%)	DBC (%)
MIX1	1.077	-	-
MIX2	1.091	-	-
pMIX1 MTS I-Al	1.141	5.9	68.1
pMIX2 MTS I-Al	1.140	4.5	27.6
pMIX1 Ivocerin	1.147	6.5	56.8
pMIX2 Ivocerin	1.146	5.0	36.9

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The table above shows the increase of density after the polymerization for both monomer mixtures and polymerization methods. When looking at the shrinkage, the GTP polymerized specimen shows lower shrinkage than the radically polymerized samples, although the DBC is lower. However, the reduction is only approximately 0.5%. In this case, the anticipated decrease in shrinkage through a controlled polymerization was partly observable, although the effect is relatively small.

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4 Summary

4.1 Two-Component (2K) GTP

With an application in the dental material industry in mind, two-component (2K) systems were examined, using Group Transfer Polymerization (GTP). GTP is a living and controlled polymerization that works at room temperature, yields polymers with narrow PDI, and enables the synthesis of well-defined polymer structures. When polymerizing difunctional monomer systems, networks with excellent homogeneity are formed that show improved mechanical properties.

In that regard, four different initiation systems for GTP were investigated in this work. In the first place, linear polymers were synthesized, using butylmethacrylate (BMA) as a monomer. The obtained polymers were characterized with GPC and NMR methods to get information about the molecular weights, molecular weight distributions, and double bond conversions. The examined systems are depicted in Figure 90. Especially the in-situ system performed very well and yielded polymers with narrow PDIs (< 1.1) and high DBCs (> 90%).

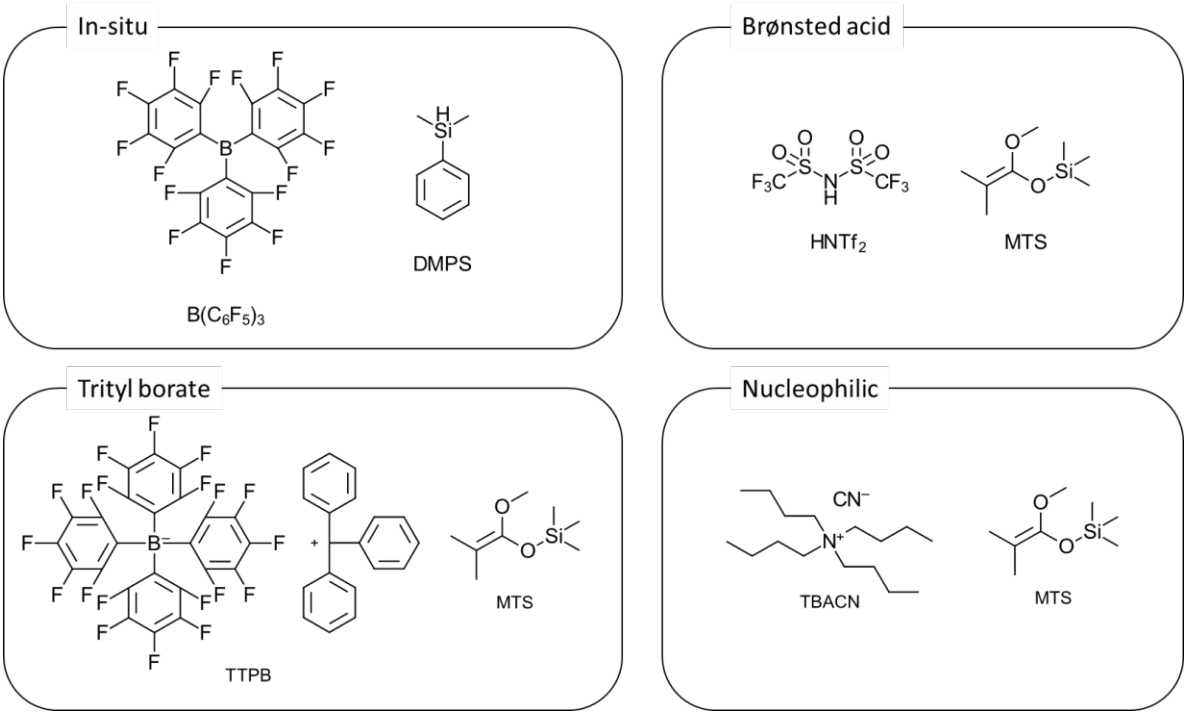

Figure 90: 2K initiating systems

In addition, difunctional systems were investigated, using typical dental monomer systems consisting of UDMA, BisGMA, and D3MA. However, none of the initiating systems was able to initiate a polymerization reaction in the UDMA and BisGMA monomer mixtures due to the presence of protic

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groups. Nevertheless, the in-situ system showed outstanding results with the monofunctional reference system and the difunctional D3MA as a monomer. For that reason, mechanical tests were performed with the in-situ system and D3MA. DMTA measurements and tensile tests, as well as density measurements were conducted and compared to a radical polymerization system. A 2K Redox system was used as a reference. A loss in mechanical properties such as Young's modulus was shown. However, the density measurements indicated less shrinkage force in the case of the in-situ system compared to the radical system. Nevertheless, the experiments showed the potential of the in-situ GTP since very low PDI polymers can be synthesized in a highly controlled way. Still, a deeper investigation has to be done to prove the reinforcing effect.

4.2 Photoinitiated GTP

Group Transfer Polymerization (GTP) presents a potent tool to include a living polymerization technique into methacrylate systems. In the dental industry, photoinitiated methacrylate systems have an essential role, which is why the GTP was employed as a photoinitiated system. A photoacid generator (I-Al) in combination with a common initiator for GTP (MTS) was used to polymerize butylmethacrylate (BMA) upon irradiation with UV light. The investigated system is depicted in Figure 91.

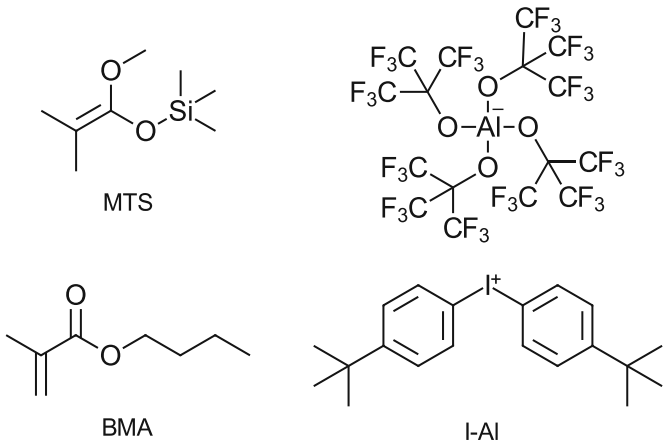

Figure 91: Monomer (BMA), initiator (MTS), and photoacid generator (catalyst, I-Al) used for photoinitiated GTP

The depicted system was investigated via Photo-DSC measurements and showed interesting results. Reproducibility of the measurements could be ensured by exclusively working inside a glovebox and measuring the respective formulations immediately after preparing them.

However, the measurements showed that besides the GTP, also radical polymerization occurs upon irradiation, which is displayed as two peaks in the Photo-DSC measurements, depicted in Figure 92.

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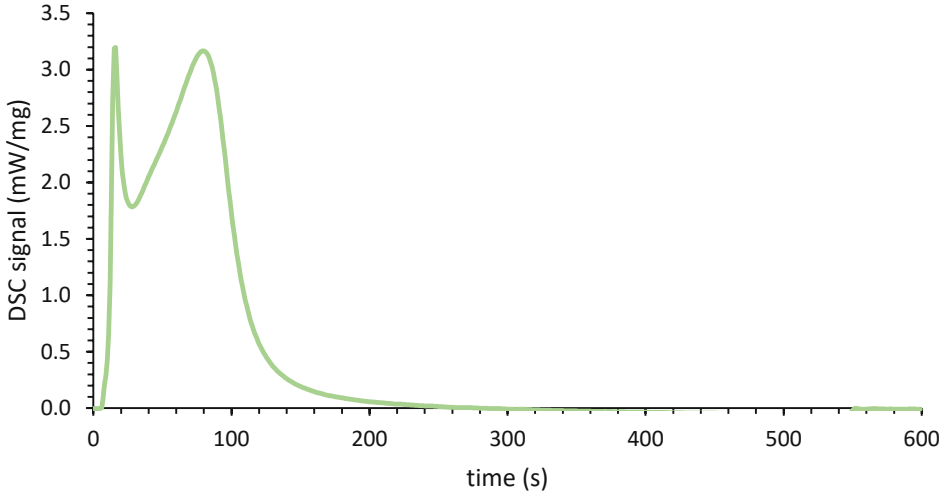

Figure 92: Photo-DSC measurement of BMA, MTS and I-Al, that shows the two observed peaks

It was assumed that the first peak is the peak that comes from the radical polymerization and the second peak from the GTP. With the use of radical inhibitor MEHQ and BHT, interestingly, the radical peak did not vanish.

In addition, difunctional monomer systems were tested with MTS and I-Al, including difunctional methacrylates without protic groups. It was shown that the higher the MTS concentration in the formulation, the higher the reactivity of the system. Furthermore, it was found that a trityl borate (Figure 93) used in literature for 2K systems showed UV absorbance similar to I-Al, however, no successful Photo-DSC measurement was possible.

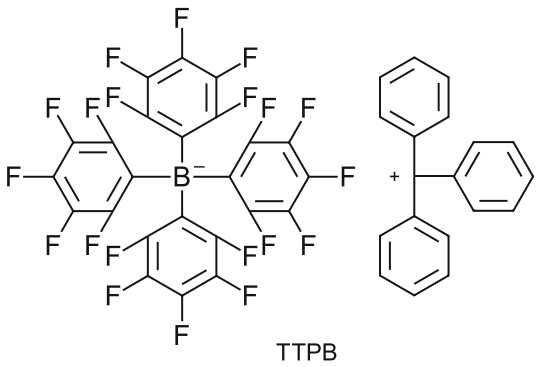

Figure 93: trityl tetrakis(pentafluorophenyl)borate (TTPB)

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The polymers obtained from the difunctional monomer systems were tested for their thermomechanical properties. For that reason, DMTA, tensile tests, and also shrinkage of the polymer specimens were measured. However, the anticipated reinforcement of the polymer network through a controlled polymerization mechanism and therefore, a homogeneous network structure could not be confirmed in this case. The GTP polymerized samples were compared to radically polymerized samples. The DMTA measurements showed that they exhibit a lower T_g and tensile tests confirmed overall lower mechanical properties. However, deeper investigation in the completely novel topic of photoinitiated GTP has to be made to optimize the systems.

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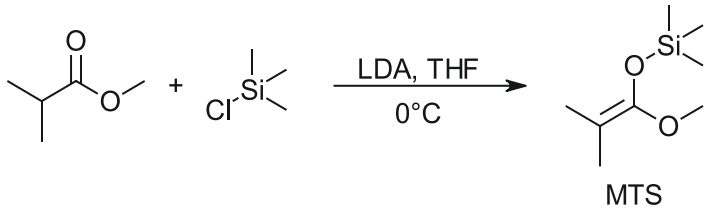
Experimental Part

2 Two-Component (2K) GTP

2.1 Linear Polymers

2.1.1 Synthesis of 1- methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS)



Name	M (g·mol^{-1})	m (g)	n (mol)	eq
BuLi	64.06	0.92	0.014	1.22
TMS chloride	108.64	2.57	0.023	2.00
diisopropylamine	101.19	1.59	0.015	1.33
methyl isobutyrate	102.13	1.21	0.011	1.00

The synthesis of MTS was performed according to literature by the reaction of methyl isobutyrate with TMS chloride. In a 3-necked 250 mL flask with a septum and stirring bar, anhydrous THF (30 mL) was cooled to -20 °C in a flask flushed with argon and diisopropylamine (5.59 mL; 0.04 mol) was added. Then buthyllithium (16 mL; 2.5M in hexane; 0.04 mol) was added and the mixture was stirred for 30 min. Next, methyl isobutyrate (3.44 mL; 0.03 mol) was added and the mixture was stirred for 1 h. Then freshly distilled TMS chloride (7.63 mL; 0.06 mol) was added and stirring was continued for another hour. The white solution was filtered, and the solvent was evaporated. The residue was treated with anhydrous diethylether (5 mL) and filtered again. The solvent was evaporated, and the residue was purified via vacuum distillation (40 mbar, bp. 68 °C).[42]

Yield: 1.41 g (68%)

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^{1}H NMR (400 MHz, chloroform-d) δ: 3.29 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H), -0.00 (s, 9H).

^{13}C NMR (101 MHz, chloroform-d) δ: 149.32 (C=$\underline{C}O_2$), 90.87 ($(CH_3)_2\underline{C}$=C), 56.50 (O-$\underline{C}H_3$), 16.46 ($\underline{C}H_3$-C), 0.00 (Si-($\underline{C}H_3$)$_3$)

2.1.2 Screening of initiating systems

The respective formulations were weighed out inside a glovebox to ensure moisture free and inert atmosphere. The catalyst was dissolved in the monomer, and the initiator was dissolved in the monomer in separate vial. The two mixtures were then mixed and polymerized.

For subsequent GPC analysis, the polymer samples inside the aluminum crucibles were dissolved in THF and passed through a syringe filter and measured afterwards. For NMR analysis, the polymer samples were dissolved in $CDCl_3$ and measured.

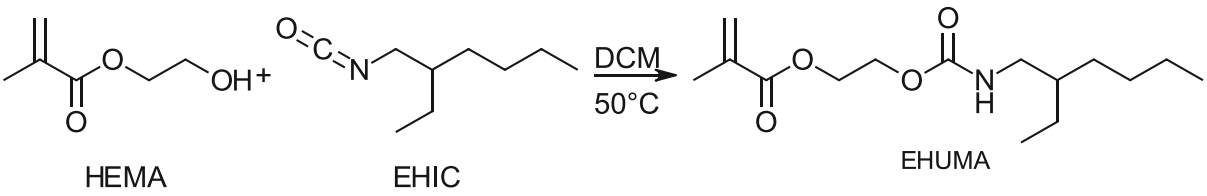
2.2 Networks

2.2.1 Screening of initiating systems

The respective formulations were weighed out inside a glovebox to ensure moisture free and inert atmosphere. The catalyst was dissolved in the monomer, and the initiator was dissolved in the monomer in separate vial. The two mixtures were then mixed and polymerized. No qualitative analysis was possible of the network.

2.2.2 Protic groups

2.2.2.1 Synthesis of Ethylhexylurethanemethacrylate (EHUMA)



Name	M (g·mol^{-1})	m (g)	n (mol)	eq
EHIC	127.18	0.26	0.0021	1.10
HEMA	130.14	0.24	0.0019	1.00

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Hydroxyethylmethacrylate (HEMA) (0.24 g, 0.0019 mol) and ethylhexylisocyanate (EHIC) (0.26 g, 0.0021 mol) were introduced to DCM in a flask under argon atmosphere. The reaction was stirred at 50 °C for 2 h. After evaporation of the solvent, the mixture was purified via column chromatography (PE:EE=3:1).[52]

Yield: 0.12 g (24%)

^{1}H NMR (400 MHz, chloroform-d) δ 6.13 (dd, 1H), 5.68 – 5.47 (m, 1H), 4.32 (s, 3H), 3.21 – 2.91 (m, 1H), 2.09 – 1.66 (m, 3H), 1.59 (s, 1H), 1.37 – 1.17 (m, 9H), 0.89 (td, J = 7.0, 2.3 Hz, 7H).

^{13}C NMR (101 MHz, chloroform-d) δ 167.20 (methacrylic C=O), 156.29 (urethane C=O), 136.02 ($CH_3\underline{C}$=C), 125.93 ($\underline{C}H_2$=C), 62.74 (d, O-$\underline{C}H_2\underline{C}H_2$-O), 43.90 (NH-$\underline{C}H_2$), 30.83 (C-$\underline{C}H_2$), 28.87 (C-$CH_2\underline{C}H_2$), 24.05 (C-$CH_2CH_2\underline{C}H_2$)

2.2.2.2 Inhibition of protic groups

Inside a glovebox 40 mg BMA and 3 mg $B(C_6F_5)_3$ were dissolved in DCM to give a 2 mol/L solution. Then, 1.6 mg DMPS was added and stirred for 40 min. An aliquot of 20 µl was extracted and quenched with a drop of methanol, then precipitated in n-hexane, filtered and dried in vacuo. GPC was measured of the obtained polymer. Another 20 mg BMA was added to the solution and stirred for 40 min, after which another GPC aliquot was pulled. Then 13 mg EHUMA or in the case of the second experiment 13 mg HEMA were added to the solution and stirred for 40 min. Again, aliquots for GPC were pulled and measured. Subsequent, another 20 mg BMA was added and stirred for 40 min, after which another aliquot for GPC was extracted and measured.

2.3 Thermomechanical tests

2.3.1 DMTA

For the DMTA measurements, specimens were prepared of the respective formulations. In the case of the 2K polymerization, the formulation was mixed and then immediately afterwards filled into the molds (sticks, 5×2×40 mm) for the DMTA specimens and cured for 1 h. This process was performed inside of a glovebox in the case of the in-situ method. The redox polymerized samples were mixed outside of a glovebox and cured in the same molds for 1 h. All the samples were then prepared with abrasive paper to ensure an even surface (< ± 0.1 mm) and comparable results.

The DMTA (dynamic mechanic thermal analysis) measurements were performed with an Anton Paar MCR 302 with a CTC 450 oven and an SRF 12 measuring system. The polymer specimens were tested

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in torsion mode with a frequency of 1 Hz and a strain of 0.1%. The temperature was increased from -100 °C to 200 °C with a heating rate of 2 °C min^{-1}. The storage modulus and the loss factor of the polymer samples were recorded with the software Rheoplus/32 V3.40 from Anton Paar.

2.3.2 Tensile tests

For the tensile tests, specimens were prepared out of the respective formulations. In the case of the 2K polymerization, the formulation was mixed and then immediately afterwards filled into the molds (dog-chew-bone specimens according to ISO 527 5b, total length of 35 mm, parallel region dimension of 2x2x12 mm) and cured for 1h. This process was performed inside of a glovebox in the case of the in-situ method. The redox polymerized samples were mixed outside of a glovebox and cured in the same molds for 1h. All the samples were then prepared with abrasive paper to ensure an even surface (< ± 0.1 mm) and comparable results. The tensile tests were performed on a Zwick Z050 with a maximum test force of 50 kN and strained with a speed of 5 mm/min. TestXpert II software was used to process and evaluate the recorded curves.

2.3.3 Density measurements

The density measurements of the solid polymer samples were conducted using a balance with a setup for weighing inside a solvent. The specimens were weighed dry first and tared. Then they were weighed under water (24 °C), and the uplift was noted. According to Equation 3 the density of measured sample could be determined.

For the density measurements of the liquid monomer mixtures, a 1 mL pycnometer was used. The weight of the pycnometer at 24 °C was noted, and the tempered liquid was transferred inside. Then, the lid with a capillary was added and any excess liquid was removed. The weight was noted again. With the difference in weight, and the exact volume of the pycnometer, the density of the liquid could be determined.

3 Photoinitiated GTP

3.1 Linear Polymers

3.1.1 Studies with MTS and I-Al

The Photo-DSC (differential scanning calorimetry) measurements were performed on a Netzsch DSC 204 F1 device with autosampler and sample holder under N_2-atmosophere. The device itself is located in an orange-light laboratory to exclude the samples from any UV-irradiation. For the measurements 12 ± 2 mg of the formulation was weighed out in aluminum crucibles. The weighing was performed inside of a glovebox to ensure moisture free and inert atmosphere. The irradiation was performed by

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an OmniCure™ series 2000 broadband Hg-lamp at 25 °C under constant N_2-atmosphere in the reaction chamber. The intensity of the irradiation was set to 35 mW/cm^2 on the samples surface. The irradiation is performed twice per sample to obtain correct results. During the measurement, the heatflow was recorded as a function of time.

For subsequent GPC analysis, the polymer samples inside the aluminum crucibles were dissolved in THF and passed through a syringe filter and measured afterwards. For NMR analysis, the polymer samples were dissolved in $CDCl_3$ and measured. The described procedure is referred to as *procedure A.*

3.1.2 Reproducibility

The respective formulations were all weighed out inside of a glovebox. The Photo-DSC measurements, GPC and NMR analysis were carried out according to *procedure A* (3.1.1).

3.1.3 Studies without MTS / without I-Al

The respective formulations were all weighed out inside of a glovebox. The Photo-DSC measurements, GPC and NMR analysis were carried out according to *procedure A* (3.1.1).

3.1.4 Radical inhibitors

The respective formulations were all weighed out inside of a glovebox. The Photo-DSC measurements, GPC and NMR analysis were carried out according to *procedure A* (3.1.1). The peak deconvolution was performed with OriginPro 2020 using an asymmetric function (Asym2Sig).

3.1.5 Storage stability

For the storage stability tests, the respective formulations were weighed out inside a glovebox and then stored under exclusion of light. The time until polymerization was noted daily and determined qualitatively.

3.2 Networks

3.2.1 Screening of catalysts

The respective formulations were all weighed out inside of a glovebox. The Photo-DSC measurements were carried out according to *procedure A* (3.1.1).

3.2.2 UV-Vis measurements

For the UV-Vis measurements of MTS, I-Al and TTPB, 1x10^{-2} mol/L, 1x10^{-3} mol/L and 1x10^{-4} mol/L solutions in acetonitrile were prepared inside a glovebox. These were then measured in a PerkinElmer Lambda 900 UV/Vis/NIR spectrometer and evaluated.

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3.2.3 UV activity of trityl salt

The respective formulations were prepared inside a glovebox. Then they were transferred inert, and cured inside a Uvitron UV oven for 10 minutes at 50% intensity.

3.2.4 Studies without MTS / without I-Al

The respective formulations were all weighed out inside of a glovebox. The Photo-DSC measurements were carried out according to *procedure A* (3.1.1).

3.2.5 Studies with different MTS / I-Al concentration

The respective formulations were all weighed out inside of a glovebox. The Photo-DSC measurements were carried out according to *procedure A* (3.1.1).

4.1 Thermomechanical tests

4.1.1 Photo-DSC

The respective formulations were all weighed out inside of a glovebox. The Photo-DSC measurements were carried out according to *procedure A* (3.1.1).

4.1.2 DMTA

For the DMTA measurements, specimens were prepared out of the respective formulations. The formulations were mixed and then immediately afterwards filled into the molds (sticks, 5×2×40 mm). The specimens for the GTP system were mixed inside a glovebox and transferred to the molds under UV light exclusion. Then they were cured inside a Uvitron UV oven for 10 minutes on each side at 50% intensity under argon atmosphere. The samples containing Ivocerin were mixed outside of a glovebox and cured under the same conditions. All the samples were then prepared with abrasive paper to ensure an even surface (< ± 0.1 mm) and comparable results. The DMTA measurement was performed according to 2.3.1.

4.1.3 Tensile Tests of the photopolymers

For the tensile tests, specimens were prepared out of the respective formulations. The formulation was mixed and then immediately afterwards filled into the molds (dog-chew-bone specimens according to ISO 527 5b, total length of 35 mm, parallel region dimension of 2x2x12 mm). The specimens for the GTP system were mixed inside a glovebox and transferred to the molds under UV light exclusion. Then they were cured inside a Uvitron UV oven for 10 minutes on each side at 50% intensity under argon atmosphere. The samples containing Ivocerin were mixed outside of a glovebox and cured under the same conditions. All the samples were then prepared with abrasive paper to

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ensure an even surface (< ± 0.1 mm) and comparable results. The tensile test measurements were performed according to 2.3.2.

4.1.4 Density measurements of the photopolymers

The density measurements were carried out according to 2.3.3.

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5 Materials and Methods

The chemicals and suppliers, that were used in the syntheses and polymerization experiments are listed in the table below.

1,10-decanedioldimethacrylate	Ivoclar AG
4-methoxyphenol	Fluka
ammonium cyanide	Aldrich
bis-(trifluormethan)-sulfonimid	TCI
bisphenol-A-glycidyldimethacrylate	Ivoclar AG
butylhydroxytoluol	Aldrich
butylmethacrylate	Aldrich
dichloromethane	Acros
diethylether	Donau Chemie
diisopropylamine	Aldrich
dimethylphenylsilane	abcr
ethylhexylisocyanate	TCI
hydroxyethylmethacrylate	Aldrich
Ivocerin	Ivoclar AG
MA-836	Ivoclar AG
methyl isobutyrate	TCI
n-butyllithium	Aldrich
tetrahydrofuran	Donau Chemie
triethyleneglycoldimethacrylate	TCI
tris(pentafluorophenyl)borate	abcr
trityl-tetrakis(pentafluorphenyl)borat	abcr
urethanedimethacrylate	Ivoclar AG
V-224	Ivoclar AG

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ATR-IR experiments of the cured specimens were performed on a PerkinElmer Spectrum 65 FT-IR Spectrometer, using a Specac MKII Golden Gate Single Reflection ATR System and evaluated with PerkinElmer Spectrum 10.03.07.0112.

Column chromatography was carried out on a Büchi Sepacore Flash System (Büchi pump module C-605, Büchi control unit C-620, Büchi UV-Photometer C-635, Büchi fraction collector C-660). Glass columns, packed with silica gel 60 (Merck, 0.040-0.063 mm were used.

DMTA was performed with an Anton Paar MCR 302 device with a CTC 450 oven. The specimens were measured in torsion mode with a frequency of 1 Hz and a strain of 0.1%. The temperature was increased from -100 °C to 200 °C with a heating rate of 2 °C/min. The glass transition temperature was defined as the temperature at the maximum of the loss factor (tan δ).

GPC measurements were carried out on a Waters GPC using 3 columns (Styragel HR 0.5, Styragel HR 3 and Styragel HR 4) and a Waters 2410 RI detector, a UV Detector Module 2550 for TDA 305 and a VISCOTEK SEC-MALS 9 light scattering detector. A calibration with polystyrene standards (375 – 177000 Da) was used to determine the molecular weight of the polymers.

NMR spectra were recorded on a Bruker DPX-200 FT-NMR spectrometer at 200 MHz for ^{1}H and 50 MHz for ^{13}C, as well as on a Bruker Avance DRX-400 FT-NMR spectrometer at 400 MHz for ^{1}H and 100 MHz for ^{13}C. The signals are recorded according to their chemical shifts, which were reported in ppm (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sep = septet, m = multiplet, bs = brad singlet) in comparison to tetramethylsilane (d = 0 ppm). The spectra were then referenced on the used NMR-solvent [^{1}H: $CDCl_3$ (7.26 ppm), ^{13}C: $CDCl_3$ (77.16 ppm)]

Photo-DSC measurements were conducted on a Photo-DSC 204 F1 from Netzsch, using 15 µ aluminum pans. An Omnicure 2000 from Lumen Dynamics with glass fiber light wave guides was used as light source, which was calibrated via an Omnicure R2000 radiometer. All measurements were conducted under N_2-atmosphere (flow rate: 20 mL/min). The data analysis was performed with the program Netzsch Proteus Thermal Analysis in version 8.0.1.

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Tensile tests were performed on a Zwick Z050 with a maximum test force of 50 kN and strained with a speed of 5 mm/min. TestXpert II software was used to process and evaluate the recorded curves.

UV-Vis measurements were performed using a Thermo Scientific™ NanoDrop™ One Microvolume UV-vis spectrometer and a PerkinElmer® Lambda900 UV/vis/NIR spectrometer.

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6 Abbreviations

2K	two-component
AFCT	addition fragmentation chain transfer
BAPO	phenyl-bis-(2,4,6-trimethylbenzoyl)-phosphinoxid
BHT	butylhydroxytoluol
BisGMA	bisphenol A-glycidyl methacrylate
BMA	butylmethacrylate
Bu	butyl-
cat.	catalyst
D3MA	1,10-decanedioldimethacrylate
DBC	doublebond conversion
DCM	dichloromethane
DMPS	dimethylphenylsilane
DMTA	dynamical mechanical thermoanalysis
EHIC	ethylhexylisocyanate
EHUMA	ethyl-hexyl-urethanemethacrylate
eq	equivalents
Et	ethyl-
G'	storage modulus
GPC	gel permeation chromatography
GTP	group transfer polymerization
HEMA	hydroxyethylmethacrylate
I-Al	iodonium aluminate catalyst
iBu	iso-butyl-
iPr	iso-propyl-
kIC	internal conversion
kisc	intersystem crossing
LDA	lithium diisopropylamine
Me	methyl-
MEHQ	methoxyphenole
MMA	methylmethacrylate
M_n	number average molecular weight
mol%	mol percent

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MTS	1- methoxy-1-(trimethylsiloxy)-2-methyl-1-propene
n.p.	no polymerization
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
pBMA	polybutylmethacrylate
PDI	polydispersity index
Peakmax	peak maximum
Ph	phenyl-
Photo-DSC	photo differential scanning calorimetry
PI	photoinitiator
PMMA	polymethylmethacrylate
S012	singlet state
SKA	silyl ketene acetal
tanδ	loss factor
TBABB	tetrabutylammonium bibenzoate
TBACN	tetrabutylammonium cyanide
TEGDMA	triethyleneglycoldimethacrylate
T_g	glass transition temperature
t_{95}	time of 95% double bond conversion
THF	tetrahydrofuran
TTPB	trityl tetrakis-(pentafluorophenyl)borat
UDMA	urethanedimethacrylate
UV-light	ultraviolet light
wt%	weight percent

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