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RESEARCH ARTICLE

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Group transfer polymerization in bulk methacrylates

Florian Pieringer[1] | **Yohann Catel**[2] | **Robert Liska**[1] | **Norbert Moszner**[2] | **Patrick Knaack**[1]

[1]Institute of Applied Synthetic Chemistry, TU Wien, Vienna, Austria

[2]Ivoclar Vivadent AG, Schaan, Bendererstrasse, Liechtenstein

Correspondence
Patrick Knaack, Institute of Applied Synthetic Chemistry, TU Wien, Vienna 1060, Austria.
Email: patrick.knaack@tuwien.ac.at

Abstract

Group transfer polymerization (GTP) is a polymerization method developed to obtain targeted (meth)acrylic polymers in solution at ambient temperatures. In this work, it is employed with methacrylic monomers to obtain low $Đ$ polymers in bulk. In this regard, different initiator systems that exhibit different mechanisms are compared concerning the molecular weight, the polydispersity and double bond conversion of the resulting bulk polymers. The respective systems were chosen carefully to give a broad overview of earlier developed initiator-catalyst combinations 1-methoxy-1-(trimethylsiloxy)-2-methylprop-1-ene (MTS) & tetrabutylammonium cyanide (TBACN) and more recently investigated initiating systems MTS & trityl *tetrakis*(pentafluorophenyl)borate (TTPB) or dimethyl phenyl silane (DMPS) & *tris*(pentafluorophenyl) borate (BCF). The described initiating systems are applied as a two-component (2K) system to ensure a homogeneous distribution of the respective initiator and catalyst in the bulk monomer. In addition to the 2K experiments, photochemical initiation is also applied to bulk formulations. Therefore, a photoacid generator (PAG) and MTS is used to trigger the polymerization reaction by irradiation with UV light. A highly controlled photopolymerization method in bulk was developed that way achieving a low polydispersity polymer with high double bond conversion.

KEYWORDS

bulk polymerization, group transfer polymerization, living polymerization, photopolymers

1 | INTRODUCTION

Group transfer polymerization (GTP) was first discovered at DuPont by Webster et al. as an alternative living polymerization technique in solution to achieve (meth)acrylic polymers with narrow polydispersity and controlled structures at ambient temperatures.[1–3] The repetitive Mukaiyama-Michael reaction is responsible for the polymerization and requires an initiating species, a silyl ketene acetal (SKA). For the activation of the SKA species, a catalyst such as Lewis acids or Lewis bases is needed to promote the polymerization reaction.[4,5] 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. Different catalysts and initiators were developed in further investigations of the new and successful method.[6–8] The variety of possible catalysts for specific

monomers is steadily growing and constant improvements are made.[9] Lewis acid catalysts are the most common, although they often require a high catalyst loading of 10–20 mol% 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 0.1 mol% relative to the initiator.[10,11] However, the exact mechanism of the polymerization reaction changes, depending on which catalyst/initiator system is used. 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-Michael reaction proceeds during the propagation.[12]

The polymerization mechanism for the nucleophilic catalyst system (Figure 1, reductive activation) divides into two postulated pathways. *Path a* refers to the associative mechanism in which the silyl group stays attached to the propagating polymer, eponymous to the GTP. *Path b* refers to a later postulated dissociative mechanism, which involves the formation of enolate anions, which are under constant complexation with another SKA molecule.[13] In the oxidative activated GTP, 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 reaction (Figure 1, oxidative activation).[14,15] Since the SKA is very unstable towards moisture, it can only be handled under inert conditions, which can cause difficulties in practical operations. A solution to that problem offers the in-situ generation of the SKA species and the simultaneous catalyzation of the GTP (Figure 1, in-situ activation). It was found by Chen et al. that BCF can catalyze the hydrosilylation of the (meth)acrylic monomer, generating a SKA species and

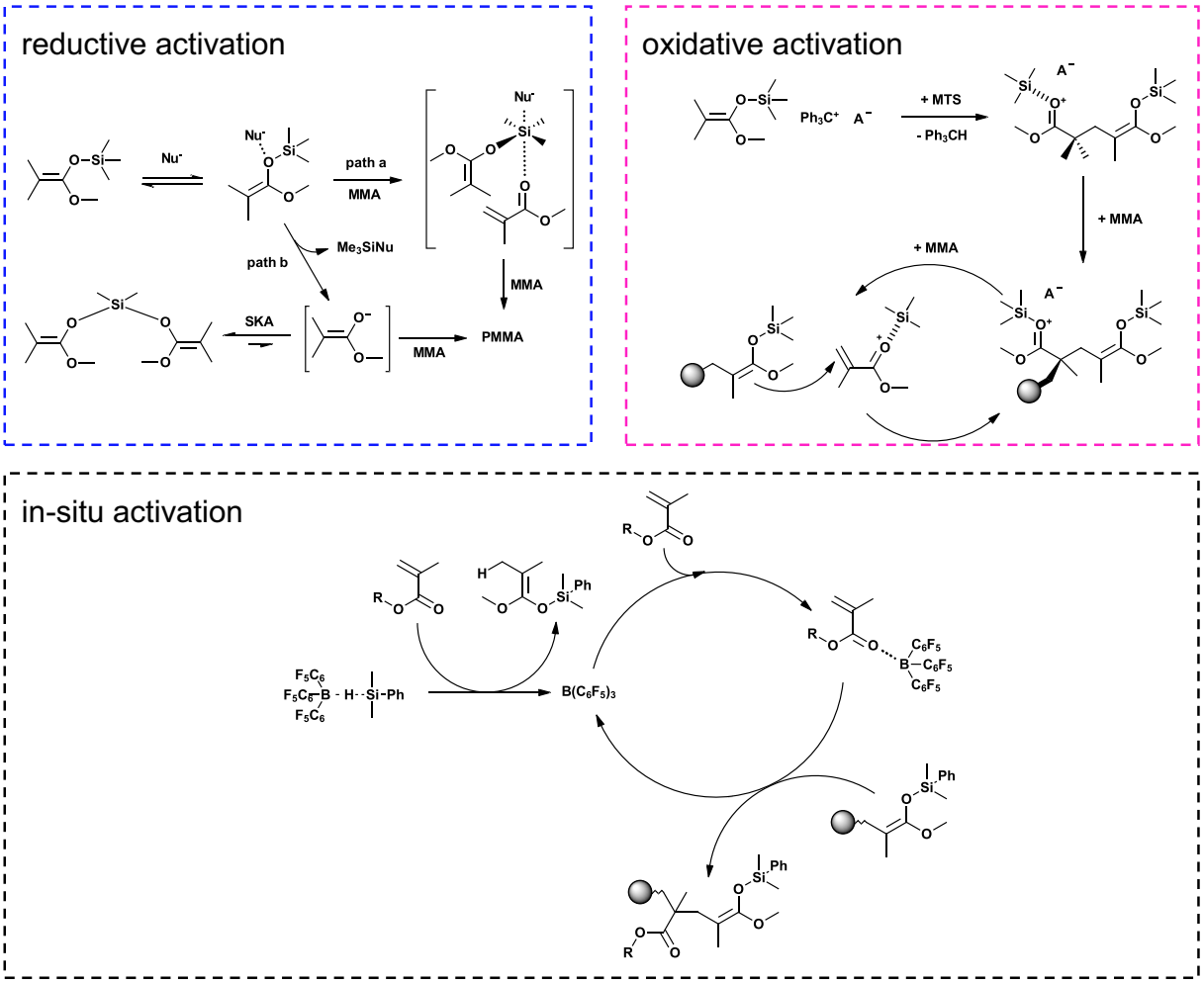

FIGURE 1 Group transfer polymerization (GTP) via reductive activation is displayed in the top left (blue dashed). The oxidative activation pathway is shown in the top right (pink dashed). The in-situ generation of silyl ketene acetal (SKA) species via the BCF-catalyzed GTP is depicted on the bottom (black dashed).[13]

promoting the GTP of the monomers in one single system. Different silanes were studied in this regard and it was found that dimethyl phenyl silane was the most effective in combination with BCF.[16,17] In an effort to open up the GTP to a much larger audience, it has to be studied not only in a solvent medium but also in the absence of solvent. Many industrial applications can handle the safety hazards of operating with polymerizations in bulk, which has not only an economic advantage but also an ecological benefit of not having to use toxic solvents. The GTP in bulk has only been studied in few details so far.[18] Patrickios et al. as well as Taton et al. are the only ones describing the polymerization of a methacrylic monomer system in bulk.[9,19,20]

Applying living polymerization techniques such as GTP in bulk monomer systems can be very beneficial, especially when adapted to multifunctional systems. It was shown that polymer networks prepared via controlled 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 obtained from the controlled polymerization method.[21]

The objective of this study is to investigate different catalyst/initiator systems applied in bulk formulations and the characterization of the resulting polymers. Also, the completely novel photoinitiated GTP was studied and successfully employed in bulk methacrylate formulations.

2 | RESULTS AND DISCUSSION

2.1 | Investigation of monomers

Since GTP is very susceptible to moisture, all experiments must be conducted under inert and water free conditions and all monomers have to be dried over molecular sieve. First, in polymerization trials with multifunctional methacrylic monomers used in industrial applications, it could be shown that monomer mixtures, in which the monomers contained protic moieties such as hydroxy- and urethane-groups, could not be polymerized via two-component bulk GTP (Table S1). However, it was shown that the same monomers showed sufficient polymerization reactivity in Photo-GTP experiments (Figure S2). It was postulated that the protic functional groups present in the monomers may exhibit an inhibitory effect on the polymerization process, similar to that of water. Therefore, the influence of these moieties on the GTP efficiency was investigated in more detail in the following experiment (Figure 2A).

The aim was to prepare a block-copolymer of *n*-BuMA and either 2-hydroxyethyl methacrylate (HEMA) or urethane methacrylate EHUMA, two monofunctional methacrylates containing a hydroxy and a urethane group (Figure 2B). For this purpose, *n*-BuMA was first polymerized in DCM solution using in-situ GTP and analyzed by GPC. To prove that the chain ends are active, *n*-BuMA was added a second time and the polymer was analyzed again by GPC. An increase in molecular weight was observed, while the polydispersity did not change. Subsequently, HEMA or EHUMA was added. In this case, no molecular weight increase could be detected by GPC, neither in the case of HEMA nor in the case of EHUMA. This observation was attributed to the deactivation of the chain ends by the protic groups of HEMA and EHUMA. It is suggested that the hydroxy-group leads to the hydrolyzation of the SKA species and the decapping of the active and living chain-ends; the same effect is attributed to the urethane group (Figure 2C). This means that no further polymerization can occur. To underline the deactivation, *n*-BuMA was added again, after which no further increase in molecular weight was observed by GPC, concluding that the polymerization was completely terminated. It could thus be shown that protic groups of monomers not only inhibit polymerization but also block the possible further reaction with other monomers by inactivating the chain ends. Therefore, the non-protic *n*-BuMA, which showed perfect reactivity towards GTP in the presented experiment was chosen as the monofunctional monomer for all further bulk experiments.

2.2 | Two-component GTP in bulk

The previously described results conclude that *n*-BuMA is a suitable monomer for two-component bulk GTP. Different generations of catalysts were studied to offer a broad view of the field of GTP. An essential premise was the solubility of the respective compounds in the bulk monomer, which limited the choice of feasible systems (Figure 3A). The behavior of bulk polymerizations can be completely different from the polymerization in a solvent environment. Indeed, the monomer has to fulfill the role of the solvent as well. In this regard, the results will be discussed in detail. Furthermore, considering that two-component systems are industrially very commonly applied, stability is often a limitation. However, in this study all experiments were conducted in a glovebox environment at room temperature, which is why no insufficient storage stability was observed.

One of the first concepts for catalyzing GTP was using bifluoride and cyanide anions.[2] To investigate these systems in bulk, the well soluble tetrabutylammonium salt TBACN was chosen as the ideal catalyst. The GTP of *n*-BuMA via the reductive activation pathway was

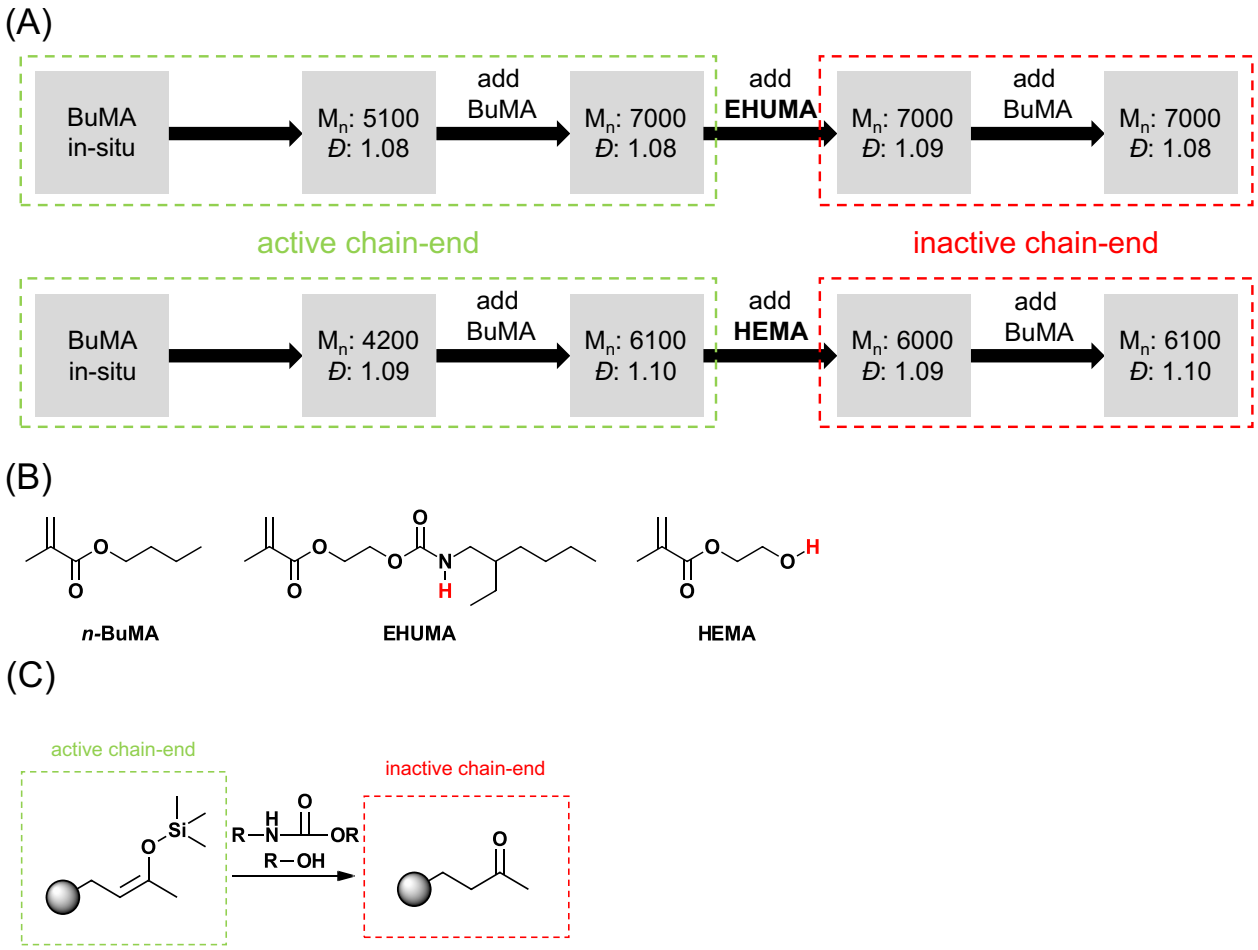

FIGURE 2 A flowchart of the experimental sequence, including GPC measurements to investigate the influence of protic moieties on group transfer polymerization (GTP), is displayed (A). Monofunctional methacrylic monomers without protic moieties (*n*-BuMA) and monomers containing hydroxy- (HEMA) or urethane- (EHUMA) groups are displayed with their protic H highlighted (B). The decapping of the living polymer chain-ends with protic moieties, such as hydroxy or urethane, is shown (C).

performed using 0.5 mol% TBACN and 1 mol% MTS referring to the number of double bonds. The induction period of the polymerization is very short (<10 s) and results in a gelled formulation in under 1 min. The fast gelation of the formulation explains the low monomer conversion observed by NMR ($DBC_{NMR} = 60\%$), shown in Table 1. If the bulk formulation gels very fast, it is difficult to achieve full conversion because the chains cannot move unhindered anymore. The molecular weight of the resulting polymer is very high ($M_n = 35.8\ kg\ mol^{-1}$) with respect to the initiator concentration, compared to a calculated $M_{n,calc}$ of $14\ kg\ mol^{-1}$. The high molecular weight also corresponds well to the observed fast gelation of the monomer formulation. The discrepancy between the theoretical $M_{n,calc}$ and the observed $M_{n,GPC}$ is explained by the low conversion of only 60% and the very fast gelation leading to longer chains due to less diffusion. Furthermore, $Đ$ is very high ($Đ = 3.2$) considering that GTP is a living polymerization and it is debatable if the polymerization is still to be considered as controlled. In the case of the reductive activation, the effect of gelation highlights the crucial difference between solvent and bulk polymerization as it only occurs in bulk formulations.

The TTPB-catalyzed GTP is reported to provide high speed living polymerization of methacrylates in solution experiments, which is why it was studied in bulk for this work.[17] The oxidative activation of the GTP via a trityl borate species of *n*-BuMA in bulk was performed using 0.5 mol% TTPB and 1 mol% MTS referring to the number of double bonds. The polymerization is proceeding much slower compared to the reductive activation with TBACN. The analyzed polymer showed a low molecular weight of $11.3\ kg\ mol^{-1}$ compared to $M_{n,calc}$ of $28\ kg\ mol^{-1}$. The oxidative activation involves a dimerization step of MTS, which lowers the number of actively initiating species to half, resulting in higher theoretical molecular weight, which highlights the importance to

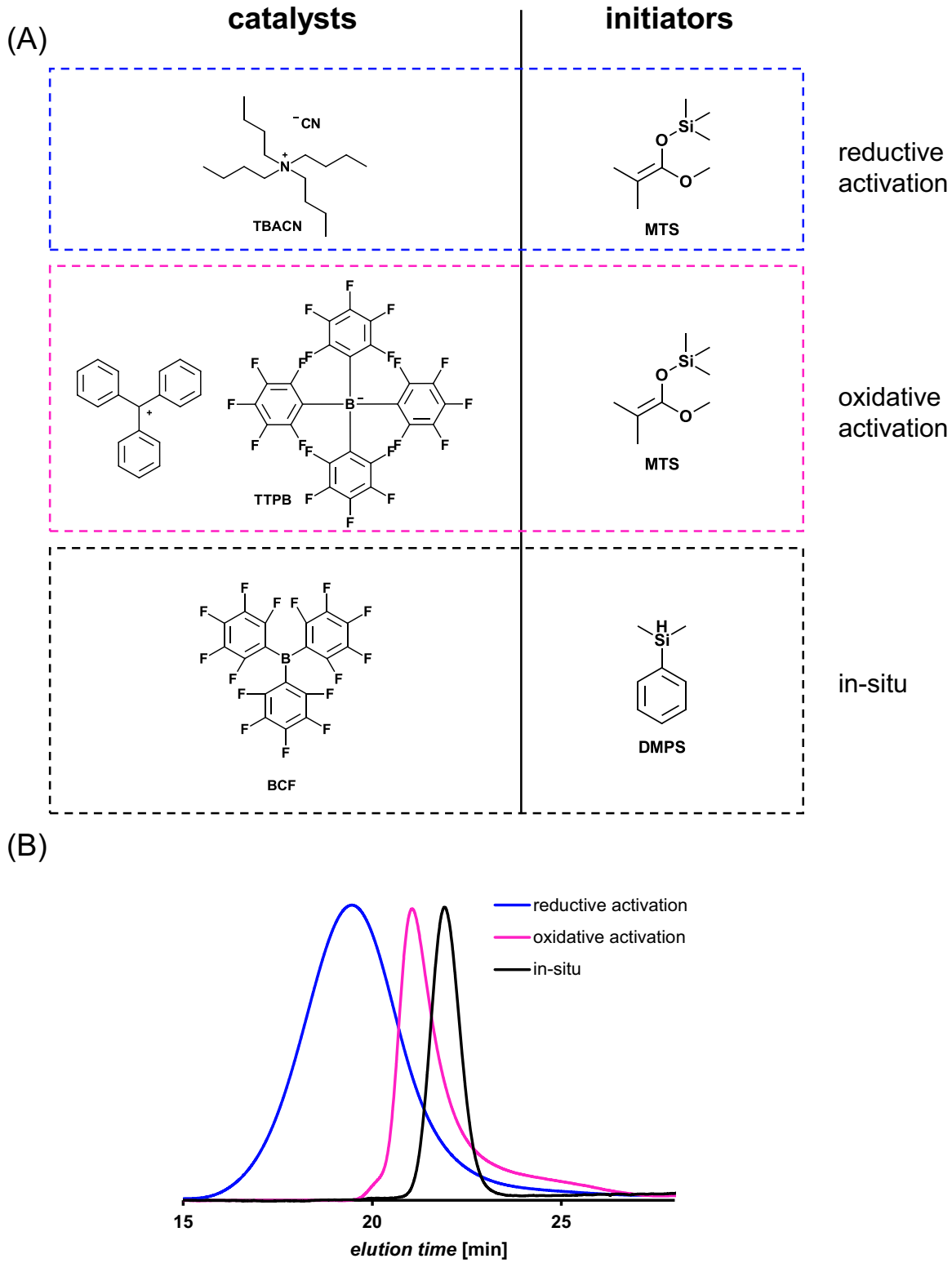

FIGURE 3 The molecular structures of the catalysts and initiators used in the 2K-polymerization experiments are shown (A). The GPC signals of the polymers made via reductive activation (blue), oxidative activation (pink) and in-situ activation (black) are displayed (B).

consider mechanistic details. The influence of this mechanism is clearly reflected in the calculated molecular weights. Referring to the peak of the GPC measurement (Figure 3B), a shift to lower molecular weights can be seen in the tailing of the peak. The formation of low molecular weight oligomers can occur due to the increasingly difficult monomer diffusion by increased viscosity of the formulation. Even though the polymerization was

TABLE 1 The measured number average molecular weight ($M_{n,GPC}$), calculated molecular weight ($M_{n,calc}$), as well as polydispersity ($Đ$) and double bond conversion via NMR (DBC_{NMR}) of the experiments employing GTP via the reductive activation (0.5 mol% TBACN and 1 mol% MTS), oxidative activation (0.5 mol % TTPB and 1 mol% MTS) and in-situ activation (2 mol% BCF and 4 mol% DMPS) are displayed.

	$M_{n,GPC}$ (kg mol^{-1})	$M_{n,calc}$ (kg mol^{-1})	$Đ_{GPC}$	DBC_{NMR} (%)
Reductive activation	35.8	14	3.2	60
Oxidative activation	11.3	28	1.9	91
In-situ	14.4	3.6	1.05	>99

conducted in bulk, a high DBC_{NMR} of 91% was achieved. The polydispersity $Đ$ is narrower ($Đ = 1.9$) compared to the reductive activation. It can be seen that the tailing of the peak is causing the broadening of the $Đ$, since the prominent peak is very narrow, therefore resulting in an overall lower molecular weight.

Using hydrosilanes is the first step to a more moisture tolerant initiation system for GTP, which is why the in-situ method employing BCF and a hydrosilane is applied here.[17] The BCF-catalyzed in-situ GTP of *n*-BuMA in bulk formulations using DMPS as the hydrosilane species was conducted using 2 mol% BCF and 4 mol% DMPS. Although it has been reported in literature that 0.5 mol% BCF and 1 mol% DMPS are sufficient, this is only referred to solution-experiments with mostly acrylates as monomers, which tend to be more reactive than methacrylates.[17] The obtained results of the analyzed polymers support the choice of catalyst and initiator concentration. The molecular weight ($M_n = 14.4$ kg mol^{-1}) of the *p*BuMA is higher than the calculated molecular weight ($M_{n,calc} = 3555$ kg mol^{-1}) while still maintaining a very narrow polydispersity ($Đ = 1.05$). The high observed molecular weight is assigned to the polymerization in bulk and especially the diffusion effects that come with it. However, the high DBC_{NMR} of >99% with the very narrow $Đ$ in the case of the BCF-catalyzed polymerization is truly remarkable considering a bulk polymerization. The in-situ generation of the initiating SKA species can evidently maintain the narrow polydispersity typical for GTP while also ensuring a very high double bond conversion. The high potential of the in-situ bulk polymerization of *n*-BuMA was subsequently used to polymerize multifunctional methacrylates. Therefore, 1,10-decandioldimethacrylate (D3MA) was used to prepare networks in bulk via the BCF-catalyzed in-situ activation obtaining a high DBC of 80%, measured by ATR-IR. The high potential of a controlled and living bulk polymerization method that can also create networks is indisputable and will show its benefits in the future. Especially in polymer materials science, the highly ordered and homogeneous networks will be of great interest and research.

2.3 | Photoinitiated GTP in bulk

In addition to the 2K systems that were previously discussed in detail, an entirely new way of initiating GTP was employed. A photoacid generator was used to release a superacid on demand via irradiation with UV light. This superacid then can activate the SKA species similar to the oxidative activation and therefore initiate the GTP (Figure S6). There is a great variety of different types of photoacid generators, including diphenyliodonium and triarylsulfonium salts of borates, antimonates, and aluminates.[22,23] Klikovits et al. reports an iodonium aluminate PAG to efficiently initiate the cationic polymerization of epoxides, which is why it was chosen as catalyst for this study.[24]

First studies using difunctional methacrylates revealed that higher concentrations of initiator and catalyst are necessary for Photo-GTP in bulk, as with low amounts no polymerization was observed (Figure S7). The shown photoinitiated GTP was conducted in an *n*-BuMA bulk formulation using 10 mol% MTS and 5 mol% iodonium aluminate (I-Al) as photoacid generator. The UV irradiation was set to 320–500 nm with an intensity of 35 mW/cm^{-2} on the samples surface and the polymerization reaction was monitored via Photo-DSC. The heat flow of the polymerization clearly shows a highly exothermic reaction right after the irradiation with UV-light starts (Figure 4, DSC-graph). The total area of the DSC curve is proportional to the total amount of heat released by the system and displayed in Table 2. However, since only a very small amount of formulation is used, no safety hazard is of concern. The ^{1}H-NMR measurement, which was performed right after the Photo-DSC experiment confirmed a high double bond conversion ($DBC_{NMR} = 95\%$). The DBC_{NMR} and $\Delta H_p = 315$ J g^{-1} was used to calculate the theoretical polymerization enthalpy for the photoinitiated GTP of methacrylates ($\Delta H_{GTP} = 47.2$ kJ mol^{-1}). This is similar to the theoretical polymerization enthalpy for radical polymerization with a literature value of $\Delta H_{p,0} = 56$ kJ mol^{-1}.[25] In addition to the high conversion, the newly developed polymerization method exhibits a very fast reaction rate indicated by the short time to the maximum of polymerization rate t_{max}. The observed t_{max} is at only 70 s and the time of 95% of the end DBC ($t_{95\%}$) is at 99 s. The bimodal peak of the shown DSC curve is due to an initial radical polymerization that is outpaced by the GTP. This radical

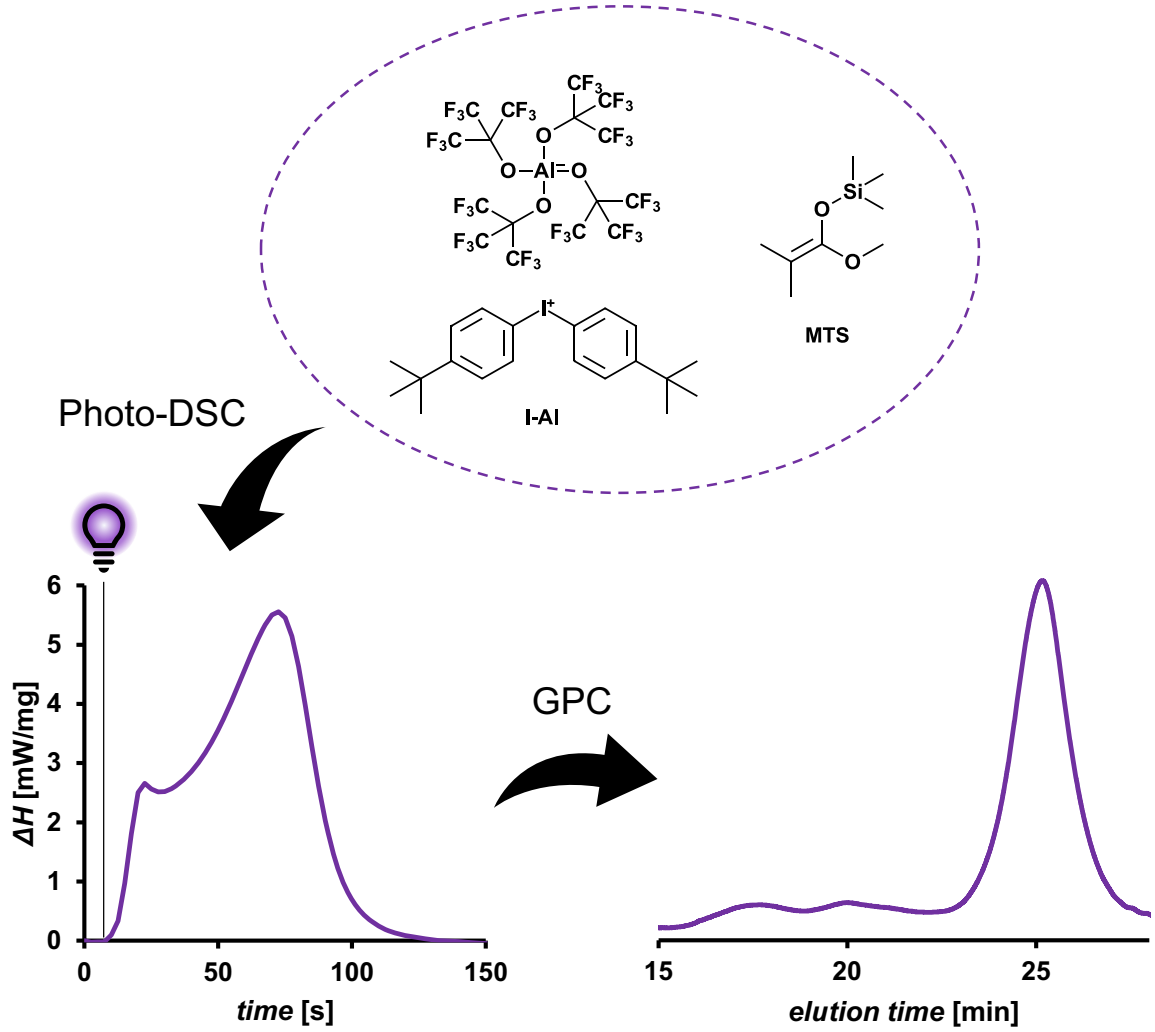

FIGURE 4 The molecular structures of the photoacid generator (PAG) and the initiator are displayed on the top. The DSC curve of the photoinitiated group transfer polymerization (GTP) is shown on the bottom left. The GPC trace of the resulting photopolymer is displayed on the bottom right.

TABLE 2 Time of peak maximum (t_{max}), time until 95% conversion is reached (t_{95}), total amount of released polymerization heat (ΔH_p) is depicted in the Photo-DSC section. Double bond conversion via NMR (DBC_{NMR}), calculated molecular weight ($M_{n,calc}$), measured molecular weight ($M_{n,GPC}$), as well as polydispersity ($Đ$) and of the photoinitiated GTP, are displayed in the polymer analysis section.

	Photo-DSC			NMR	GPC		
	t_{max} (s)	t_{95} (s)	ΔH_p (J g^{-1})	DBC_{NMR} (%)	$M_{n,calc}$ (kg mol^{-1})	$M_{n,GPC}$ (kg mol^{-1})	$Đ$
Photo-GTP	70	99	315	95	1.4	3.2	1.19

polymerization is likely caused by the formation of radicals during the homolytic cleavage of the PAG. However, it was shown that successful Photo-GTP is only possible if the SKA and PAG are both present during irradiation (Figure S8). These results are also reflected in the obtained GPC measurement (Figure 4, GPC-graph). There are traces of very high molecular weight polymer at lower elution times (17–22 min) attributed to the low amounts of radically polymerized monomer, however, the prominent peak is the very narrow peak of the GTP-polymer. The molecular weight ($M_{n,GPC} = 3.2$ kg mol^{-1}) is approximately double the calculated molecular weight ($M_{n,calc} = 1.4$ kg mol^{-1}), which is explained by a similar mechanism to the oxidative activation. If a dimerization process of SKA is involved in the mechanism, the observed molecular weight will double. The controlled polymerization process is also maintained and reflected in the low polydispersity ($Đ = 1.19$).

3 | CONCLUSION

In summary, we studied different monomers for their compatibility with group transfer polymerization, focusing on protic moieties. We could show that protic moieties are inhibiting the polymerization reaction and additionally completely deactivating it for further polymerization. Moreover, *n*-BuMA was polymerized in bulk with different GTP initiating systems, comparing the mechanism of reductive activation, oxidative activation, and in-situ activation. We were able to obtain a highly controlled, low polydispersity (<1.2) and high DBC polymerization reaction with a bulk formulation as well as network formation. Additionally, the newly developed GTP initiating method via a photoacid generator was proven to provide high DBC and low polydispersity (<1.2) polymers upon irradiation with UV light, opening up a new approach to creating highly ordered photopolymers. To the best of our knowledge, this is the first time a low polydispersity and simultaneously high DBC polymer is obtained via a photoinitiated group transfer polymerization. These results introduce an entirely new field of photopolymerization, utilizing GTP for a highly controlled and fast bulk polymerization of *n*-BuMA.

4 | EXPERIMENTAL SECTION/METHODS

4.1 | Materials

Bis[4-(*tert*-butyl)phenyl]iodonium *tetra*(nonafluoro-*tert*-butoxy)aluminate (Synthon), 2-ethylhexyl-isocyanate (98%, Aldrich), diisopropylamine (≥99%, Aldrich), dimethyl phenyl silane (97%, abcr), hydroxyethyl methacrylate (≥99%, Aldrich), methyl isobutyrate (≥99%, TCI), *n*-butyllithium (2.5 M in *n*-hexane, Aldrich), *n*-butyl methacrylate (99%, Aldrich), tetrabutylammonium cyanide (95%, Aldrich), tris(pentaflurophenyl)borane (95%, abcr) and trityl tetrakis(pentafluorophenyl)borate (97%, abcr) were used as received. For the polymerization experiments, the used monomers were dried over molecular sieve (3 Å) and stored inside a glovebox. All solvents were used as received without further purification.

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

The synthesis of MTS was performed according to literature by the reaction of methyl isobutyrate with TMS chloride.[26] 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 *n*-butyllithium (16 mL; 2.5 M 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 diethyl ether (5 mL) and filtered again. The solvent was evaporated, and the residue was purified via vacuum distillation (40 mbar, bp. 68°C) to yield a colorless liquid (yield: 68%). ^{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-($\underline{C}H_3$)$_3$).

4.3 | Synthesis of 2-(2-Ethylhexylaminocarbonyloxy)ethyl-methacrylate (EHUMA)

The synthesis of EHUMA was performed according to the literature.[27] Hydroxyethyl methacrylate (0.24 g, 0.0019 mol) and ethylhexyl isocyanate (0.26 g, 0.0021 mol) were introduced to DCM in a flask under an 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) to yield a colorless liquid (yield 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-$CH_2CH_2\underline{C}H_2$).

4.4 | Influence of protic moieties on GTP

Inside a glovebox, 40 mg *n*-BuMA and 3 mg BCF were dissolved in dry DCM to give a 2 mol L^{-1} solution. Then, 1.6 mg DMPS was added and stirred for 1 h. 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 *n*-BuMA was added to the solution and stirred for 1 h, 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 1 h. Again, aliquots for GPC were pulled

and measured. Subsequently, another 20 mg *n*-BuMA was added and stirred for 1 h, after which another aliquot for GPC was extracted and measured.

4.5 | 2K-system polymerization procedure

For each polymerization experiment, the respective amount of catalyst was weighed out in a glass vial inside a glovebox to ensure a completely dry and oxygen-free atmosphere and dissolved in *n*-butyl methacrylate monomer. Likewise, the initiator was weighed in a glass vial inside a glovebox and dissolved in *n*-butyl methacrylate monomer. Subsequently, the respective catalyst and the initiator formulation were mixed in a 1:1 ratio and homogenized. The bulk polymerization yielded solid *p*BuMA for all performed experiments and could be taken for further analysis. For subsequent GPC analysis, 2 mg of the polymer were dissolved in 2 mL THF and passed through a syringe filter. For NMR analysis, 10 mg of the polymer samples were dissolved in $CDCl_3$ and measured.

4.6 | Photoinitiated polymerization procedure

The Photo-DSC measurements were performed on a Netzsch DSC 204 F1 device with autosampler and sample holder under N_2-atmosphere. The device is located in an orange-light laboratory to exclude the samples from UV irradiation. For the measurements, 12 ± 2 mg of the formulation was weighed in aluminum crucibles. The weighing was performed inside a glovebox to ensure a moisture-free and inert atmosphere. The irradiation was performed by an OmniCure™ series 2000 broadband Hg-lamp with a 320–500 nm filter at 25°C under a constant N_2-atmosphere in the reaction chamber. The intensity of the irradiation was set to 35 mW/cm^2 on the surface of the sample. During the measurement, the heat flow was recorded as a function of time. For subsequent GPC analysis, 2 mg of the polymer was dissolved in 2 mL THF and passed through a syringe filter. For NMR analysis, 10 mg of the polymer samples were dissolved in $CDCl_3$ and measured.

4.7 | Polymer characterization

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)]. 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. 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 (375–177,000 Da) was used to determine the molecular weight of the polymers.

ORCID

Florian Pieringer https://orcid.org/0000-0002-3337-7088
Robert Liska https://orcid.org/0000-0001-7865-1936
Norbert Moszner https://orcid.org/0000-0002-9854-1838
Patrick Knaack https://orcid.org/0000-0001-9984-9087

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