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PAPER

Successful radical induced cationic frontal polymerization of epoxy-based monomers by C−C labile compounds†

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Thermal bulk curing of epoxy resins is a non-energy efficient method. On the other hand classical photo-curing techniques for epoxy resins are limited to quite thin layers, due to the limited penetration depth of UV-light. We show that Radical Induced Cationic Frontal Polymerization (**RICFP**) is a promising technique for the energy efficient bulk curing of epoxy resins. The combination of a C−C labile compound (1,1,2,2-tetraphenylethanediol) as a thermal radical initiator with diaryliodonium salts results upon local thermal- or photoinitiation in a self-sustaining front moving along the formulation and curing cationically curable resins completely. This allows the curing of monomer formulations in places that are not easily accessible or on objects that cannot be thermally cured because of their thermal instability or size. In this paper we report about first basic investigations on **RICFP** of several epoxy resins with C−C-labile compounds and compare them to common thermal radical initiators.

Introduction

Epoxy resins are one of the most important functional monomers and prepolymers that can be polymerized *via* a cationic pathway. The diglycidyl ether of bisphenol A (**BADGE**) is among the most widespread used in industry (Fig. 1). In 2009 1 093 000 tons of **BADGE** polymers were produced over the world. The **BADGE** polymers are used for surface coatings, bonding and adhesives, flooring constructions, composites, electrical and electronic laminates, embedding and tooling and other applications.[1]

Curing of **BADGE** polymers is usually performed by polyaddition of amines, anhydrides or phenolic compounds with polymerization accelerators on the base of heavy metal carbonic acid salts like Zn-naphthenate. This curing process

Fig. 1 Structure of the bisphenol A diglycidylether resin (**BADGE**).

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involves usually the heating of the monomer formulation to elevated temperatures of about 140 °C to accelerate the polymerization.[2]

Cationic photopolymerization is a suitable method for a more energy efficient hardening of epoxy resins. Cationic polymerization also works with different kinds of monomers *e.g.* oxetanes or vinyl-ethers. To start the polymerization cationic photo acid generators like sulphonium- or iodonium salts, or in some cases the less efficient ferrocenium salts are very commonly used initiators.[3] The disadvantage of the common photocuring of epoxy resins is that it only works in thin films and not in bulk.

For energy efficient curing in bulk and to speed up the curing process alternative curing methods for hardening of **BADGE**-based formulations are of interest. For this purpose the application of frontal polymerization is a very promising approach.

Frontal polymerization (**FP**) is a method to produce polymers, characterized by a self-sustaining reaction front, which moves once initiated through a reaction vessel (Fig. 2). The reaction heat produced by the polymerization leads to the decomposition of thermo-labile initiators which start further polymerization reactions in their surroundings. However a front can only be sustained if the heat loss is low enough, so that enough energy is available to cleave further initiators.

This effect was firstly described in the seventies of the 20th century by Chechilo and Enikolopyan.[4] Since then a broad spectrum of research has been carried out on this field covering many types of monomers, initiators and different polymer-
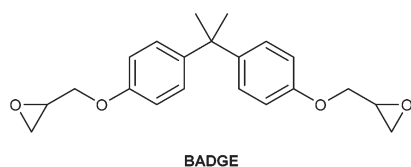
Fig. 2 Scheme of a photo initiated thermal frontal polymerization.

ization reactions (*i.e.* free radical, cationic, *etc.*). A good overview about the topic of frontal polymerization is provided by Pojman in a recent review and paper.[5,6]

The initiation process of the **FP** can be started either by irradiation with light or by local application of heat. Therefore one speaks of thermal- or photo-induced thermal frontal polymerization. In this paper only the background of photo-induced thermal frontal polymerization has been discussed. In general one can differentiate between two types of photo-induced thermal frontal polymerization: radical and cationic photopolymerization. Although both types involve the formation of radicals during the process the difference is the mechanism of the polymer formation.

In the field of epoxy-monomers Scognamillo *et al.* describe the frontal polymerization of trimethylolpropane triglycidyl-ethers with commercially available borontrifluoride initiators in combination with amines.[7,8] This leads to thermally induced bulk polymerization with a moving reaction front and allows different types of filler materials. Very intensive investigations have been performed by Crivello *et al.* concerning the cationic frontal polymerizations of oxetanes and epoxides, which have been monitored by optical pyrometry.[9–11] Also hybrid frontal polymerization consisting of epoxide/oxetane and acrylate monomers were analysed by Crivello.[12] All these publications have in common that, they do not comply with the definition of a thermal frontal polymerization

stated by Pojman, since they involve the irradiation of the entire formulation *e.g.* to produce a photoacid release and initiate the polymerization afterwards by local application of heat. This means that the cationic reactive species is already present in the formulation prior to the initiation and therefore not generated during the reaction as described by Pojman.[5] The disadvantage of the aforementioned techniques using light induction is the requirement of being able to irradiate all the surfaces of the formulations and limits the thickness of the cured samples depending on the penetration depth of the light. To circumvent this limitation the combination of the radical induced decomposition of cationic initiators and frontal polymerization is a very promising approach.

The principle of radical induced cationic polymerization (**RICP**) is already known for a while.[13–15]

In the case of a radical induced cationic frontal polymerization (**RICFP**) the photoinitiator also gets cleaved by irradiation and forms a cation. This cation abstracts a proton from a monomer or the solvent and therefore forms a highly reactive super acid as shown in Scheme 1. In step 2 of this scheme the super acid reacts with a monomer forming a polymer and generates heat. The produced heat will subsequently cleave the thermal radical initiator producing reactive radicals which on their part can cleave the cationic (photo) initiator and form further acid (step 3 and 4). That starts the exothermic polymerization in the adjacent region (Fig. 2).

Currently there is only one publication that combines the concept of **RICP** and **FP** leading to a front which is kept alive by the radicals built from the thermal radical initiator. Mariani *et al.* showed that the combination of an epoxy monomer (**CE**) with dibenzoyl peroxide (**BPO**) and an iodonium salt (**HOPH SbF₆**) leads to systems that were able to polymerize thick samples.[16]

Mariani *et al.* used a cyclohexyl epoxy ester (**CE**) compound as the resin for the curing of thick samples and showed that both photochemical (**HOPH SbF₆**) and thermal (**BPO**) initiators are necessary for a successful and complete curing (Fig. 3).

Scheme 1 Cationic photo frontal polymerization on the example of an iodonium salt as photoinitiator.
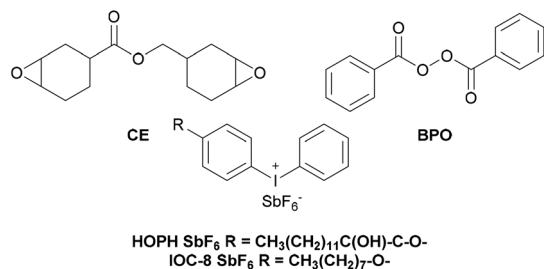
Fig. 3 Chemicals used by Mariani et al. for curing thick epoxy samples.

Due to the widespread industrial use of **BADGE** we focused our research on the investigation of its behaviour in **RICFP**. For this purpose a large variety of thermal radical initiators were screened, together with several photoacid generators and finally the best system was also tested on a bunch of epoxy based resins for its applicability.

Results and discussion

Setup for RICFP

The setup for the evaluation of **RICFP** consists of a mould for the polymerization made from poly(tetrafluoroethylene) (**PTFE**), a lightguide and UV source for the initiation of the polymerization, thermocouples and a camera for the analysis of the front properties (Fig. S1†). The front is conducted horizontally along a length of 70 mm with a constant width of 10 mm and the mould is 5 mm deep (Fig. S2†). The initiation is performed on one end of the mould on an area of about 1 cm² with UV-light of 320 to 500 nm (Fig. 4).

Basic investigations about BADGE and CE for RICFP

In our basic study we wanted to analyse the eligibility of the resin bisphenol A diglycidyl ether (**BADGE**) which is an industrially widely used epoxy resin.
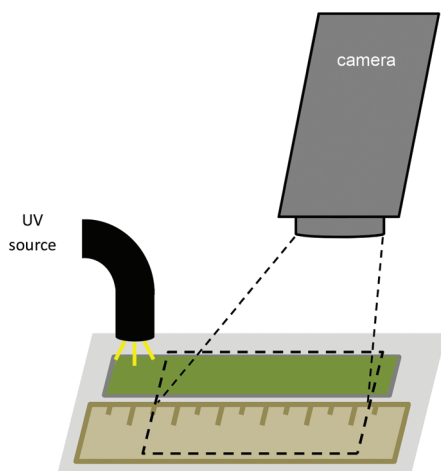
Fig. 4 Schematic view of a horizontal frontal polymerization setup.

According to Mariani et al. the common thermal initiator **BPO** is a suitable radical initiator for **RICFP** in combination with iodonium salts and the epoxy monomer **CE**. Based on this study **BPO** was also examined for its suitability in combination with the cationic initiator **IOC-8 SbF$_6$** (which is very similar to Marianis **HOPH SbF$_6$**) and **BADGE**. Similar to Mariani et al. we selected **BPO** as the thermal radical source.

The feasibility of **RICFP** with **CE** and **BPO** as initiators as claimed in the work of Mariani could be well confirmed. However in our case we observed some undesired gas formation which might be ascribed either to the decarboxylation reaction of the formed radical or due to breakup of the ester-group in the **CE** monomer.

However with the usage of **BADGE** as the monomer the formation of a front was not possible with **BPO** (1 mol%) and **IOC-8 SbF$_6$** (1 mol%). A local polymerization in the pathway of the UV light could be detected but no further polymerization occurred. Therefore the concentration of **BPO** was increased stepwise up to 10 mol% (equivalent to about 7 wt%) with the same negative result. Also the structure relative dilauroylperoxide (**DLPO**, $T_{1/2, \ 10h}$ = 65 °C) was tested for its applicability – which failed too to form a front.

In the next step radical thermal initiators with comparable half-life temperatures: dicumylperoxide (**DCPO**, $T_{1/2, \ 10h}$ = 115 °C), tert-butylperoxide (**TBPO**, $T_{1/2, \ 10h}$ = 125 °C) and 1,1-di-(tert-butylperoxy)-3,3,5-trimethylcyclohexane (**TBPTC**, $T_{1/2, \ 10h}$ = 85 °C) and also the less stable percarbonate bis(4-(tert-butyl)-cyclohexyl) peroxydicarbonate (**TBC-PDC**, $T_{1/2, \ 10h}$ ∼ 40 °C) were investigated. These initiators cover a wide range of thermal stability with half-life temperatures between 40 and 125 °C, but also these initiators were not able to give the frontal polymerization with **BADGE** as the resin.

Finally a complete different type of thermal radical initiator was tried – azobis(isobutyronitrile) (**AIBN**, $T_{1/2, \ 10h}$ = 65 °C). **AIBN** is a non-peroxide based initiator with a half-life temperature of about 65 °C. This initiator on the one hand should be reactive enough and on the other hand be different in its reaction mechanism to so far tested initiators. Despite that, it turned out that **AIBN** is also not suitable for the **RICFP** of **BADGE**.

A member of a completely different group of thermal radical initiators is benzopinacol (1,1,2,2-tetraphenylethanediol, **TPED**). It belongs to the group of carbon–carbon labile compounds that undergo cleavage of the C–C bond upon elevated temperatures forming carbon centered radicals. A half-life temperature of **TPED** could neither be found in the literature nor determined via DSC. This is most likely because the radicals will recombine with the pinacol if there are no reaction partners and therefore no heat flow is generated (Scheme 2). Although C–C labile compounds are known as high temperature radical initiators[17] it showed that the combination of **BADGE** with 1 mol% of the thermal initiator TPED and 1 mol% of the cationic initiator **IOC-8 SbF$_6$** gives a formulation that undergoes perfect **RICFP**. A video of the above mentioned formulation undergoing **RICFP** can be found in the ESI.†
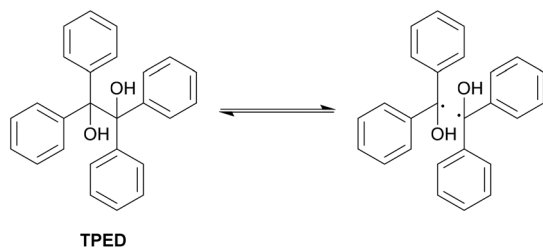
Scheme 2 Cleavage and recombination of C–C labile **TPED**.

To confirm that **TPED** is the only initiator that allows **RICFP** all other thermal initiators were also tested in the double amount of 2 mol%. Unfortunately none of them worked out. To confirm **RICFP** of the **TPED** based systems experiments without thermal or without cationic initiators were performed. In both cases no front could be observed.

C–C labile compounds

To explore the structural requirement for C–C labile compounds in **RICFP** a few other initiators similar to **TPED** were investigated (Fig. 5). The nitrile **TPE-CN** and the tetraphenylethane **TPEH** are different from **TPED** concerning the lacking oxygen atoms but still have the tetra-phenyl structure and should be C–C labile compounds. They have been investigated towards their applicability as radical initiators in papers from Braun.[18,19] In **TPED-Si** the free OH groups are silylated but apart from that it has the same structure as **TPED**. To the third group of relatives belongs **TPAP** which is quite different from the **TPED** structure but also bears four phenyl rings which would weaken the C–C bond. Additionally the structure contains a benzoyl chromophore well known for high reactivity in classical type I photoinitiators. It is known from Baumann *et al.* that **TPAP** also forms radicals upon heating.[20]

It could be shown that the oxygen bearing species **TPED** and **TPED-Si** are able to produce a frontal polymerization whereas all other components were not able to start the front. Additionally to the experiments with 1 mol% of each initiator, they were also performed with 2 mol% of each initiator with the similar result. It seems that the presence of the alcohol groups is necessary for the successful frontal polymerization of **BADGE**. Currently it cannot be ruled out that the trimethylsilyl (**TMS**) protected pinacol **TPED-Si** is hydrolyzed by the

superacid during the polymerization process and forms the alcohol **TPED** as the reactive species. This topic needs a more comprehensive study which would go beyond the scope of this work and will be covered in a future study.

Cationic initiators

Since cationic polymerization cannot only be carried out with iodonium hexafluoroantimonate two alternatives have been tested. The perfluorphenylborate based iodonium salt **IPTI-PFPB** is a commercially available high-end photoinitiator with very good performance bearing the advantage that during hydrolysis no fluoride ions are formed (Fig. 6). Its drawback is the rather complicated synthesis with explosive pentafluorophenyllithium intermediates. It was tested in 1 mol% concentration together with 1 mol% of **TPED** and it also turned out to be suitable for **RICFP**. Since it is rather expensive compared with **IOC-8 SbF₆** it has no significant benefits for its use in this study and is therefore only used as the proof of concept.

IPTI-PFPB
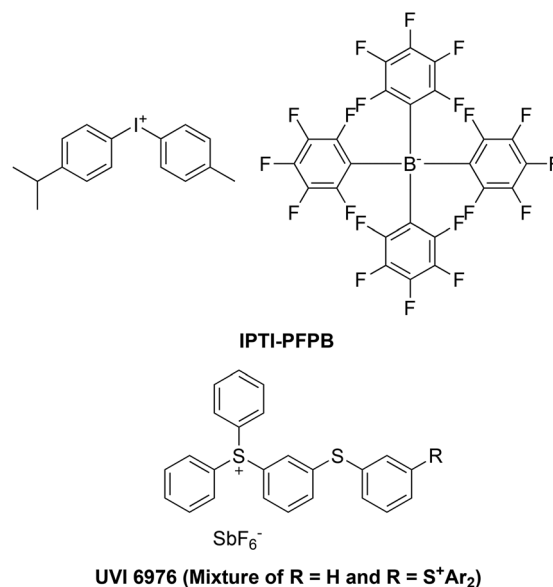
UVI 6976 (Mixture of R = H and R = S⁺Ar₂)

Fig. 6 Structure of the iodonium based photoacid generators with borate based counterion and structure of the triarylsulphonium based commercial photoinitiator UVI 6976, which is a mixture of at least those two species dissolved in propylene carbonate.
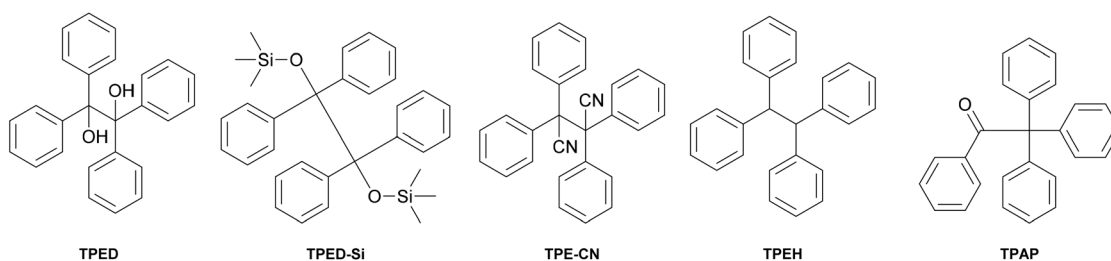

Fig. 5 Structures of C–C labile compounds and structure relatives which were tested as thermal initiators for **RICFP**.

An alternative type of photoacid generators are the widespread used triaryl sulphonium salts with a chromophore that shifts the absorption well above 300 nm. They have a slight disadvantage of producing bad odors due to the resulting sulfide species generated upon initiation. They are provided in solution in propylene carbonate which makes mixing with resins easier.

For the experiment the commercially available cationic photoinitiator **UVI 6976** which consists of a mixture of two different triarylsulphonium salt species dissolved in propylene carbonate was used. Since the exact ratio between the two species is not known it was not possible to determine the molar concentration of the initiator in comparison with the resin.

Therefore concentration of the triarylsulphonium initiator was increased up to 5 wt% and even with this concentration no front could be achieved. According to Yagci iodonium salts are more prone to oxidize radicals than sulphonium salts because of their higher redox potential.[21] The oxidation of the radicals leads to the decomposition of the onium salt and therefore leads to the acid formation. Here it seems that the lower redox potential of sulphonium salts may be the reason why the latter are not applicable for the frontal polymerization of **BADGE** in combination with the thermal initiator **TPED**.

Resins

The primary scope of this work was to develop a new technique for the curing of **BADGE**-based formulations. Since this works very well with the combination of the C–C labile compound **TPED** and the iodonium salt **IOC-8 SbF₆** this combination was also analysed towards their applicability for **RICFP** with three other epoxy-based resins. The glycidylethers neopentanediol diglycidylether (**NPDGE**), hexanediol diglycidylether (**HDDGE**) and cyclohexanedimethanol (**HDDGE**) should possess a higher reactivity compared to **BADGE** due to their lower molecular weight in a ratio to their number of reactive groups (Fig. 7).

The experiments were conducted with **IOC-8 SbF₆** and **TPED** in 1 mol% concentration. Although a **RICFP** was possible with all resins listed here the produced polymers of

NPDGE, **HDDGE**, **CHDGE** and **CE** show certain bubble formation presumably due to the high front temperature.

Nevertheless, the frontal polymerization experiments were analyzed concerning the velocity of the front and the maximum frontal temperature. The velocity of the front (V_F) was determined by recording the polymerization process with a camera and a ruler alongside the polymerization pathway.

As can be seen from Fig. 8 the graph is strictly linear which is characteristic for frontal polymerizations. From the slope of the line one can calculate the velocity in cm min^{-1}. The velocity strongly depends on the used resin and the concentration of the initiators.

The temperature during the reaction is monitored *via* three thermocouples which are inserted perpendicular to the front direction and positioned with their tip in the mid of the mould. The first thermocouple is useful for recognizing the start of the frontal polymerization because in the case of a starting front the temperature will raise erratically and not just gradually from the irradiation. This also leads to higher temperature indicated by the first thermocouple located directly in the pathway of the UV light. For the analysis of the maximum front temperature ($T_{F,max}$) the maximum values from the second and third thermocouple, located in the area of steady state front reaction, which vary only slightly (±5 °C), were averaged.
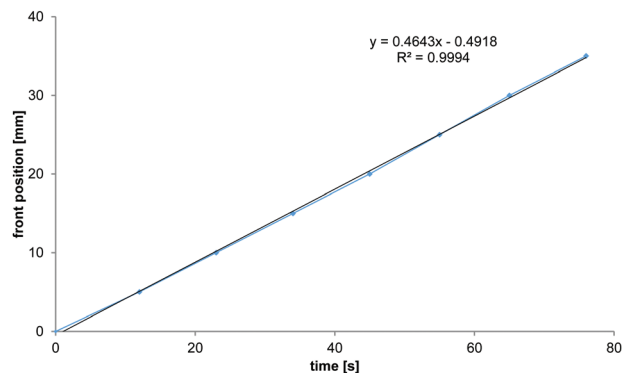

Fig. 8 Example how the front velocity is determined based on front position and time in case of formulation consisting of BADGE with 1 mol% of **TPED** and **IOC-8 SbF₆** each.
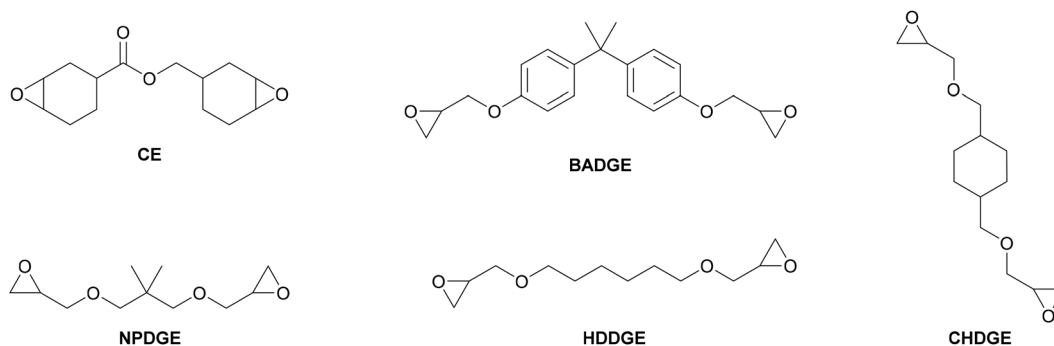

Fig. 7 Structures of resins which have been successfully polymerized *via* RICFP.

Table 1 Front parameters of different resins polymerized *via* RICFP

Resin	$T_{F,max}$ [°C]	V_F [cm min^{-1}]	t_{start} [s]
BADGE	173	2.7	38
NPDGE	169	19.9	10
CE	176	26.2	31
HDDGE[a]	181	28.6	12
CHDGE	140	37.9	23

[a] Velocity approximated due to nonlinear front behavior.

The front starting time (t_{start}) is defined as the time from the beginning of the irradiation until the front is visibly moving beneath the metal screen (detailed information on the setup can be found in the ESI†).

As can be seen in Table 1 the front temperature is located between 140 °C and almost 200 °C depending on the resin. The biggest difference in the front velocity shows the comparison of **BADGE** with the extremely reactive **CHDGE** which shows almost 15 times faster front propagation. Although the velocity of 2.7 cm min^{-1} seems quite low, **BADGE** is the only monomer that results in a dense and well-shaped polymer – all others form foamy bubble-rich polymers.

Experimental

Materials

BADGE (Araldite MY 790-1, Huntsman), cyclohexanedimethanol diglycidylether (**CHDGE**, PolyPox R11, UPPC), 1,6-hexanediol-diglycidylether (**HDDGE**, PolyPox R18, UPPC) and 1,3-bis-(2,3-epoxypropoxy)-2,2-dimethylpropane (**NPDGE**, PolyPox R14, UPPC) were kindly provided as gift. 1,1,2,2-Tetraphenyl-1,2-ethandiol (**TPED**, Fluka) p(octyloxyphenyl)phenyliodonium hexafluoroantimonate (**IOC-8 SbF$_6$**, ABCR), (4-isopropylphenyl)-(*p*-tolyl)iodonium tetrakis(perfluorophenyl)borate (**IPTI-PFPB**, ABCR), 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (**CE**, Sigma-Aldrich) were purchased and used as received. 2,2,3,3-Tetraphenylsuccinonitrile (**TPE-CN**),[22] 1,1,2,2-tetraphenylethane (**TPEH**),[23] and 2,2,7,7-tetramethyl-4,4,5,5-tetraphenyl-3,6-dioxa-2,7-disilaoctane (**TPED-Si**)[24] were synthesized according to the literature.

Frontal polymerization

Sample preparation and setup. A typical formulation for 3 runs of frontal polymerization consists of 15 g **BADGE** resin (44 mmol), 0.163 g **TPED** (1 mol%) and 0.287 g **IOC-8 SbF$_6$** (1 mol%). The initiators were dissolved in as little methylene chloride as possible (typically 3 mL) and mixed with the resin. Thereafter the methylene chloride was removed under vacuum (about 0.03 mbar) for at least two hours and to keep the **BADGE** resin in the liquid state the formulations were stored on a 50 °C water bath. As soon as the bubble formation has ceased the formulation can be transferred to the mould (Fig. S1†). All other formulations were conducted accordingly.

Since there is a strong dependence of the front temperature from the amount of resin in the mould, the resin is always weighed (typically 3.5 g) to be sure that the mass is always the same.

For evaluation of the frontal polymerization a mould made out of poly(tetrafluoroethylene) (**PTFE**) was used. The size of the cavity is 70 × 10 × 5 mm and has 6 horizontal slots for inserting thermocouples. For this experiment the thermocouples were always situated in position 1, 3 and 6 – 1 is directly under the light guide. Pictures of the actual polymerization setup as well a detailed blueprints of the mould can be found in the ESI (Fig. S1 and S2†).

Irradiation of the sample formulations is performed with an Omnicure Series 2000 by Lumen Dynamics and an 8 mm light guide with a 320–500 nm filter and a light intensity of ~500 mW cm^{-2} at the surface of the formulation. The distance from the tip of the lightguide to the formulation was constant, 5 mm. An area of about 1 cm^2 was irradiated while the rest of the formulation was shielded from the UV light by a stainless steel slide. A ruler is placed alongside the mould to analyse the front velocity.

The reaction gets initiated by irradiation with UV-light and the irradiation is stopped as soon as the front passes the metal screen. Observation of the polymerization is made with a webcam and thermocouples so that the front temperature as well as the front velocity can be analysed after each run. All polymerizations were run in triplicates and the results were averaged.

Analysis of the frontal parameters

For the analysis of the front velocity the polymerization process is recorded with a LifeCam Cinema Webcam from Microsoft.

The position of the front is determined every 5 mm together with time since the start of the irradiation. This data points are plotted to a curve whose slope is determined by regression. The slope of the curve matches the velocity of the polymerization front.

For the recording of the temperature three K-type thermocouples together with a Pico TC-08 USB Logger (AD converter) is used. The software PicoLog Recorder of version 5.23.0 was used to record and convert the data for further usage. Since the temperature from the first thermocouple (direct beneath the light guide) is usually higher because of the irradiation energy, these values were not included. The temperatures from second and third thermocouple were averaged.

Conclusions

It could be shown that radical induced cationic frontal polymerization (**RICFP**) of **BADGE**-based resin formulations is a suitable way for energy efficient curing of bulk materials. We developed a system for the evaluation of thermal frontal polymerization in terms of front velocity, front temperature and front starting time. Only the use of C–C labile thermal

initiators like the tetraphenylethanediol **TPED** leads to clear and solid polymers. Besides the leading substance **TPED** a large bunch of other radical initiators have been tested for its applicability and it showed that only **TPED** and its silyl-capped version **TPED-Si** are suitable for **RICFP** of **BADGE**-based formulations. Also other glycidylether-based monomers like **NPDGE**, **HDDGE** or **CHDGE** or the cycloaliphatic epoxide **CE** are possible to cure in a frontal polymerization with the hereby described system. Hence this innovative approach of a bubble free frontal polymerization of epoxy-based resin offers great potential for further fundamental and applied research.

Acknowledgements

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