Supplementary information: Novel thermal initiator systems for radical induced cationic frontal polymerization

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1 Setup for frontal polymerization experiments
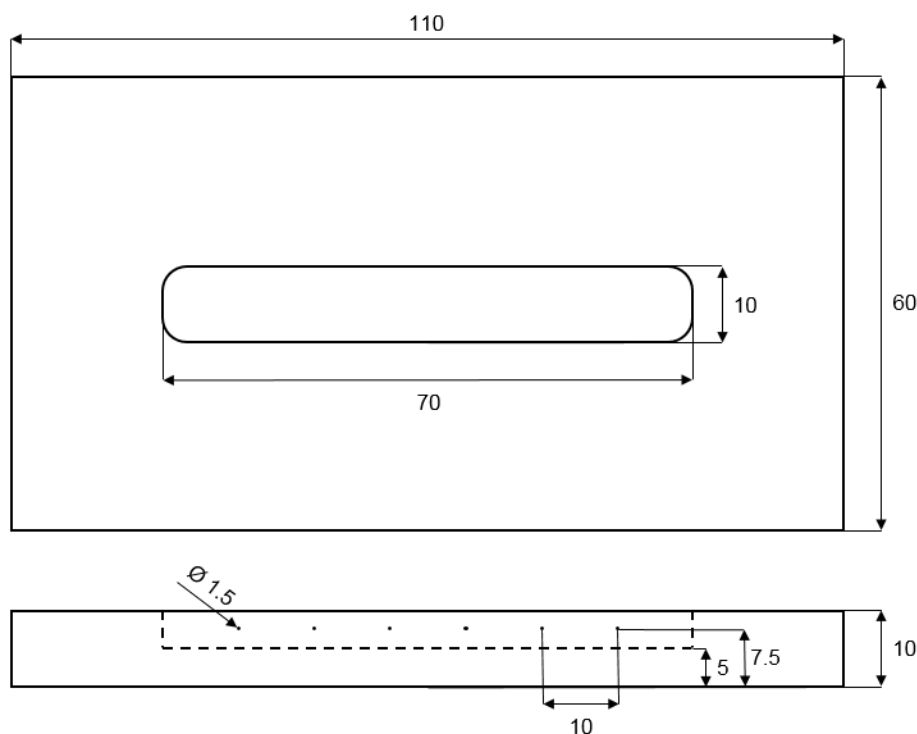
1.1 PTFE mold

Figure S1: Dimensioned drawing of the PTFE mold used for the frontal polymerization tests.

The frontal polymerization experiments were carried out in a PTFE mold (Figure S1). The mold contains a cavity for applying the resin and six holes on the side, which serve as guides for thermocouples. Guides that are not used are closed with small pins.

1.2 Setup B

In setup B, a universal clamp is used instead of the light guide holder to fix the light guide 1 cm above the sample surface. The guides for the thermocouples are all closed with small pins and an infrared camera is mounted centrally above the setup to record the experiments. As in setup A the polymerization is initiated using a 320-500 nm UV light

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source calibrated to give an intensity of around 320 mW/cm² at the surface of the sample. A schematic illustration of setup B is given in Figure S2.
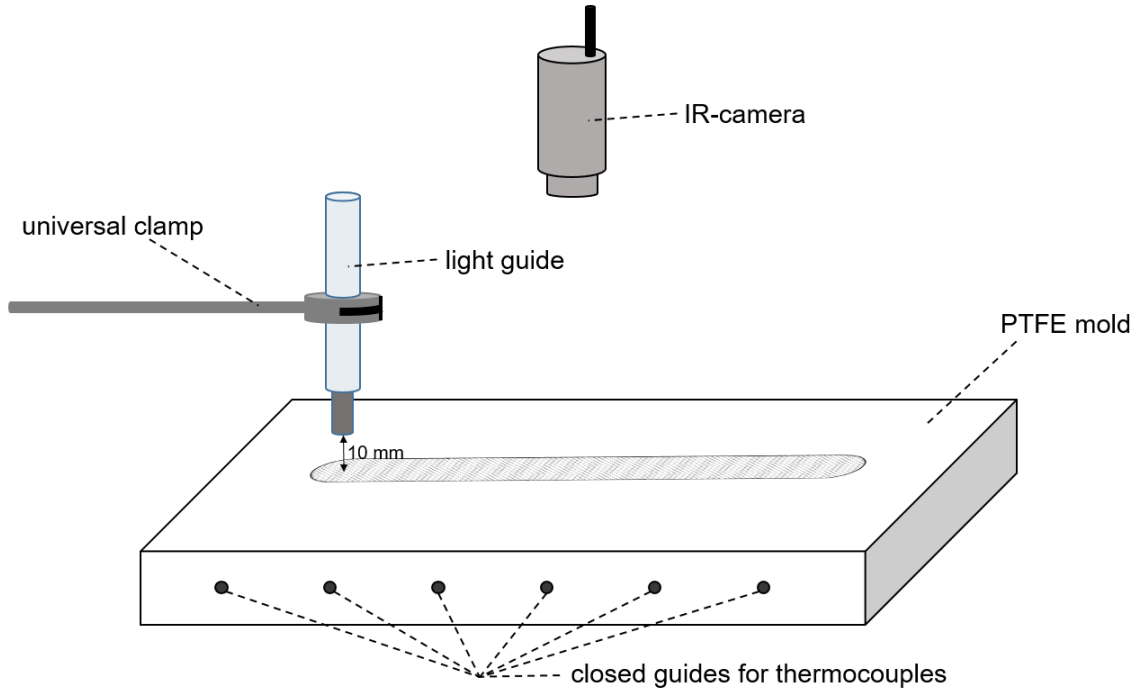

Figure S2: Schematic illustration of Setup B.

1.3 Determination of the frontal parameters

1.3.1 Starting time (t_S)

Since in setup A the polymerization front is not visible from the beginning, the start time must be determined via formula 1. The time (t) is measured until the front is visible for the first time after the irradiation shield. The previously determined front velocity (v_F) is used to determine how long the front needs to move the distance (d) between the starting point and the irradiation shield. This duration is then subtracted from the previously measured time (t) to determine the actual start time (t_S).

$$t_S = t - \frac{d}{v_F} = 30\ s - \frac{10\ mm}{0.42\frac{mm}{s}} = 6.19\ s \tag{1}$$

The starting time in setup B is determined using a stopwatch. The time is measured from the point when the light source is switched on until the front starts moving.

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1.3.2 Front velocity (v_F)

To determine the frontal velocity (v_F), distance-time diagrams were created. The stated velocities are derived from the slope of fitted regression lines.

When using setup A, this diagram is created by taking the time of the recorded video whenever the front has moved 5 mm.

In setup B, a grid with ten consecutive squares of 10x10 pixels is placed over the frontal polymerization setup in the software of the IR camera. Before the experiment, a preheated metal plate with a slit of exactly 21 mm is measured in pixels in the software to determine the conversion factor between pixels and mm. The distance-time diagram is created in the same way as with setup A, but in this case the time is measured every 10 pixels and the distance is then converted from pixel in mm.

An example of the evaluation of an experiment carried out with setup B is shown in Table S1 and Figure S3. In this example, the slope of the regression line is 0.42, which means that the v_F is 0.42 mm/s, corresponding to 2.52 cm/min.

Table S1: Measured values for an exemplary evaluation of a frontal polymerization experiment.

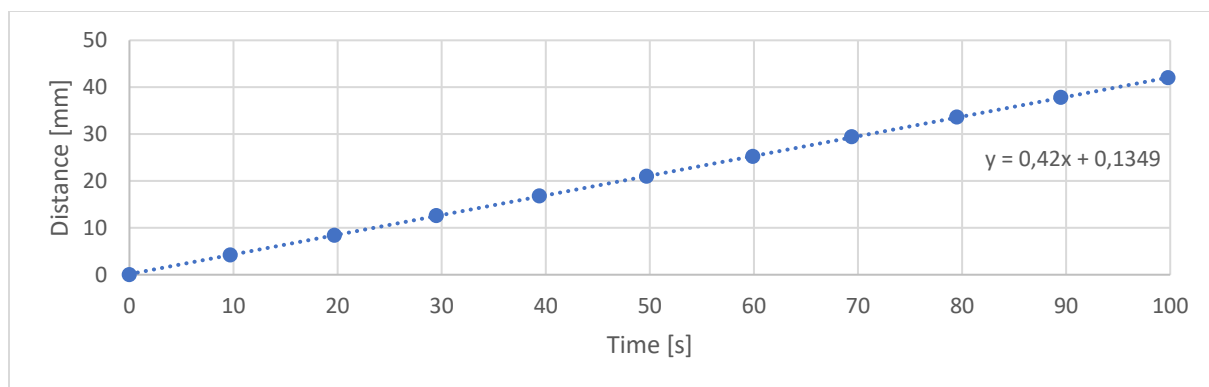| Distance [pixel]	Distance [mm]	Time [s]
0	0	0
10	4.2	9.7
20	8.4	19.7
30	12.6	29.5
40	16.8	39.4
50	21	49.7
60	25.2	59.9
70	29.4	69.4
80	33.6	79.5
90	37.8	89.5
100	42	99.8

Figure S3: Example for a distance-time diagram for the evaluation of the front velocity (v$_F$).

1.3.3   Front temperature (T$_F$)

In setup A, the temperature is measured with 1.5 mm thick thermocouples in the positions 1, 4 and 6. To determine the front temperature (T$_F$), however, the maximum values from positions 4 and 6 are used and averaged. Higher temperatures are measured at position 1, since more heat is released at once when the reaction is started with the light source. Therefore, this value is not taken into account. As the thick thermocouples appear to dissipate heat, the values measured with them are lower than those measured with the IR camera in setup B.

In setup B, the highest mean temperatures of each 10 x 10-pixel square through which the front passes completely are averaged to determine the front temperature.

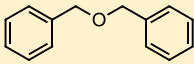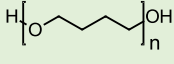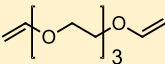## 2   Carbon-based coinitiators for RICFP

The assumed initiation mechanism of the carbon-based coinitiators is shown in the main part of the publication in Figure 5. The key points are the hydrogen transfer from the coinitiator to the oxygen radical of the RTI and the oxidation of the resulting carbon radical by the PAG.
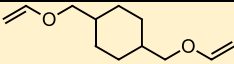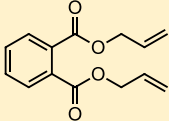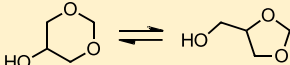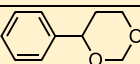
Mainly, oxygen-containing hydrocarbon compounds were chosen as coinitiators. This choice was influenced partly by the promising characteristics of THF and n-butyl vinyl ether in the literature and partly due to the fact that the highly efficient radical produced during TPED cleavage also includes oxygen bonded to carbon.

Since the RTI BPO is poorly soluble in the monomer BADGE and gas development was observed in some experiments with higher initiator concentrations, DCP was selected as RTI for these experiments. As preliminary tests indicated a relatively low reactivity when combining DCP with carbon-based coinitiators, the initiator concentration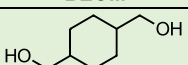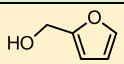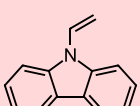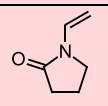 was doubled compared to the silane systems. The formulations used, therefore, consist of 1 mol% DCP, 2 mol% of the respective carbon-based coinitiator, 0.1 mol% PAG and the monomer BADGE.

For the evaluation of these systems setup B was used. All carbon-based coinitiators tested and the corresponding results of the frontal polymerization experiments are summarized in Table S2. In the experiments marked with ~, a certain propagation of the front was observed, but this was not stable and did not spread through the entire resin. Nevertheless, the front parameters were determined for these experiments. The front velocities (v_F) stated here (marked with *), however, are not comparable with the others. As these could only be determined relatively close to the light source, they are higher due to the additional energy input. Furthermore, the provided front temperatures for these experiments may be unreliable, as there are typically fewer values available for accurate determination.

Table S2: Structures of the used carbon based coinitiators and results of the frontal polymerization experiments. The prepared formulations for these experiments contain 2.0 mol% coinitiator, 1.0 mol% DCP, 0.1 mol% PAG and BADGE.

	Coinitiator	Frontal polymerization	v_F [cm/min]	T_F [°C]	t_S [s]
0	-	~✗	2.29*	202.2	17
1	Tetrahydrofuran **THF**	✓	2.05	207.8	16
2	Dibenzyl ether **DBE**	~	2.28*	199.6	13
3	Poly(tetrahydrofuran) [1000] **PolyTHF**	✓	2.25	199.7	36
4	Tri(ethylene glycol)divinyl ether **TEGDVE**	~	1.47*	172.1	27

	Coinitiator	Frontal polymerization	v_F [cm/min]	T_F [°C]	t_S [s]
5	1,4-Cyclohexanedimethanol divinyl ether **CHDVE**	~	2.11*	204.0	12
6	Diallyl phthalate **DAP**	~	1.92*	198.6	13
7	1,3-Benzodioxole **BDO**	✓	2.15	211.4	11
8	Glycerol formal **GF**	~	2.80*	217.2	11
9	4-Phenyl-1,3-dioxane **PDO**	~	2.42*	199.0	12
10	3-Ethyl-3-oxetanemethanol **EOM**	✓	2.37	219.9	9
11	3,3'-[Oxybis(methylene)bis-(3-ethyloxethane) **BEOM**	✓	1.69	207.9	9
12	1,4-Cyclohexanedimethanol **CHDM**	✓	2.40	214.9	8
13	Furfuryl alcohol **FFA**	~	2.87*	170.85	9
14	9-Vinylcarbazol **VC**	✗	-	-	-
15	1-Vinyl-2-pyrrolidinone **VP**	✗	-	-	-

* Values are slightly too high since the energy input due to the light induction causes a higher starting speed.

Surprisingly, a short propagation of the front was also observed in the blank sample (**0**) without coinitiator, but nevertheless no stable frontal polymerization was achieved. Perhaps this might be explained by the fact that hydrogen atoms could also be abstracted at the monomer BADGE, which would make it act as a coinitator itself. In this case, however, BADGE does not seem to be a very efficient coinitiator. Stable frontal polymerizations were obtained with the ether-based coinitiators THF (**1**) and polyTHF (**3**), but not with BDE (**2**). In the case of the vinyl- and allyl-ether-based ones (**4-6**), no satisfactory results could be achieved, which is why this substance class appears to be unsuitable as a coinitiator. For the actales (**7-9**), stable frontal polymerization could only be achieved with BDO. The two oxetanes (**10**, **11**) used also yielded stable frontal polymerization, with EOM (**10**) having a significantly higher frontal velocity than BEOM (**11**). The diol CHDM (**12**) delivers the highest frontal speed of all suitable coinitiators used. In general, coinitiators with alcohol moiety may cause slightly higher frontal velocities as can be seen, for example, in the comparison between EOM (**10**) and BEOM (**11**) or PolyTHF (**3**) and THF (**1**). To actually confirm this, however, further tests would have to be carried out.

3 Picture of a cured polymer sample

Figure S4: Picture of a cured polymer sample consisting of 1.0 mol% TTMSS, 0.5 mol% BPO, 0.1 mol% PAG and BADGE.