Supporting information

Blue light-induced iniferter RAFT polymerization in aqueous-alcoholic media as a universal tool for the homopolymerization of various monomer families: kinetic investigations in different scales

Lara Hub[a,b], Joachim Koll[a], Maryam Radjabian[a*], Volker Abetz[a,b*]

a) Helmholtz-Zentrum Hereon, Institute of Membrane Research, Max-Planck-Straße 1, 21502 Geesthacht, Germany. E-mail: maryam.radjabian@hereon.de

b) Institute of Physical Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany. E-mail: volker.abetz@uni-hamburg.de

1. Absorption spectrum of the RAFT agent DDMAT

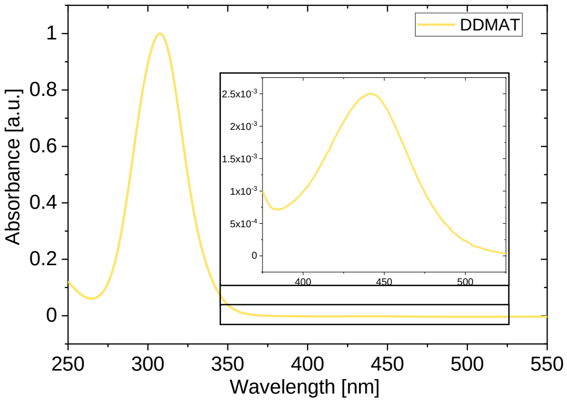

Fig. S 1: UV-Vis absorption spectrum of the RAFT agent DDMAT in ethanol. The signal with the maximum at 308 nm shows the spin-allowed π → π* electronic transition, the second absorption region with the local maximum at 442 nm is assigned to the spin forbidden n → π* electronic transition.

2. Photoreactor set-up

2.1 Experimental set-up

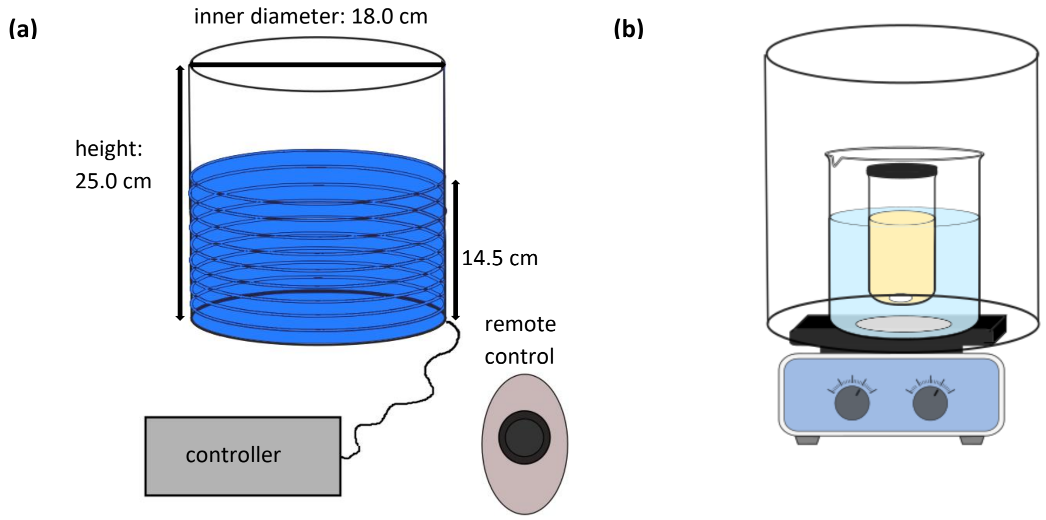

Fig. S 2: (a) Schematic set-up of the photoreactor. (b) Schematic experimental set-up for blue light initiated RAFT polymerizations. The polymerization vessels were placed into a water bath centered on the heating plate (not to scale).

2.2 Light intensity of the photoreactor

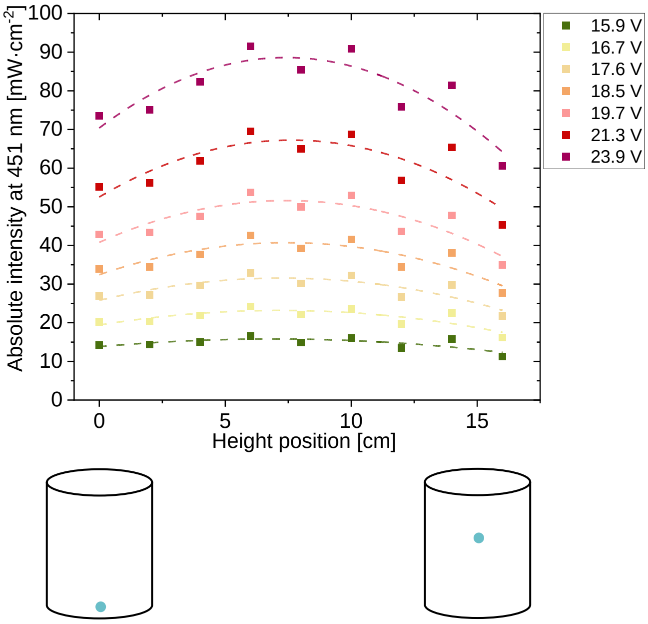

Fig. S 3: Height position dependent light intensity of the blue LED at the maximum emission wavelength of $\lambda_{\max} = 451$ nm at the centre of the blue LED.

3. Synthesis of PDMAEA, P4VP and P2VP macroCTAs *via* blue light-induced iniferter RAFT solution polymerization

Synthesis of PDMAEA macroCTA *via* blue light-induced iniferter RAFT solution polymerization. A typical photo-iniferter RAFT polymerization of DMAEA with a molar ratio of $[\text{DMAEA}]_0/[\text{DDMAT}]_0 = 500/1$ was conducted as follows: DDMAT (10.0 mg, 27.4 µmol, 1.0 eq.) and DMAEA (2.22 mL, 13.7 mmol, 500 eq.) were dissolved in ethanol (5.34 mL). While stirring the solution, water (4.22 mL) was added dropwise and *N*,*N*-dimethylformamide (20 µL) added as an internal reference for ^{1}H-NMR analysis and an initial sample was taken. The solution was degassed by purging the ice-cooled polymerization vial with argon for 10 min. The polymerization vessel was placed in the centre of the photoreactor and the polymerization was carried out under blue light irradiation (λ_{max} = 451 nm) at a water bath temperature of 40 °C under constant stirring (400 rpm). After the desired time of exposure to the blue light, the polymerization was stopped by turning off the irradiation source, quenching in an ice-cooling bath and exposing to air. The solvent was removed by vacuum and the crude polymer was obtained by drying in vacuum at 40 °C for 24 h. Subsequently, the polymer was dissolved in ethanol, precipitated in cold cyclohexane, filtered and dried under vacuum at 40 °C for 48 h.

Synthesis of P4VP macroCTA *via* blue light-induced iniferter RAFT solution polymerization. A typical RAFT photopolymerization of 4-vinylpyridine with a molar ratio of $[\text{4VP}]_0/[\text{DDMAT}]_0 = 470/1$ was conducted as follows: DDMAT (30.0 mg, 82.3 µmol, 1.0 eq.) and 4VP (4.19 mL, 38.9 mmL, 471 eq.) were dissolved in ethanol (10.41 mL) and stirred for homogenization. Water (8.23 mL) was added dropwise. The reaction solution was degassed by purging the ice-cooled polymerization vial with argon for 10 min. The polymerization vial was placed in the water bath with a temperature of 40 °C or 50 °C and illuminated with blue light (λ_{max} = 451 nm). After the desired time of exposure to the blue light, the polymerization was stopped by turning-off the irradiation source, quenching in an ice-cooling bath and exposing to air. The solvent was removed by vacuum and the crude polymer was obtained by drying in vacuum at 40 °C for 24 h. Subsequently, the polymer was dissolved in ethanol, precipitated in cold cyclohexane, filtered and dried under vacuum at 40 °C for 48 h.

Synthesis of P2VP macroCTA *via* blue light-induced iniferter RAFT solution polymerization. In a typical photo-iniferter RAFT polymerization of 2VP with a molar ratio of $[\text{2VP}]_0/[\text{DDMAT}]_0 = 470/1$, DDMAT (35.0 mg, 96.0 µmol, 1.0 eq.) and 2VP (4.89 mL, 45.3 mmol, 470 eq.) were dissolved in ethanol (7.09 mL). Under stirring conditions, water (5.60 mL) was added. The cooled solution was degassed by purging with argon for 10 min. The polymerization vessel was placed in the centre of the photoreactor and the polymerization was conducted under constant stirring (400 rpm) and started by placing the vial in the water bath (40 °C – 70 °C) and exposing the solution to blue light (λ_{max} = 451 nm). After the desired time of exposure to the blue light, the polymerization was stopped by turning-off the irradiation source, quenching in an ice-cooling bath and exposing to air. The solvent was removed by vacuum and the crude polymer was obtained by drying in vacuum at 40 °C for 24 h. Subsequently, the polymer was dissolved in ethanol, precipitated in cold cyclohexane, filtered and dried under vacuum at 40 °C for 48 h.

4. NMR analysis

4.1 Determination of the DMA conversion

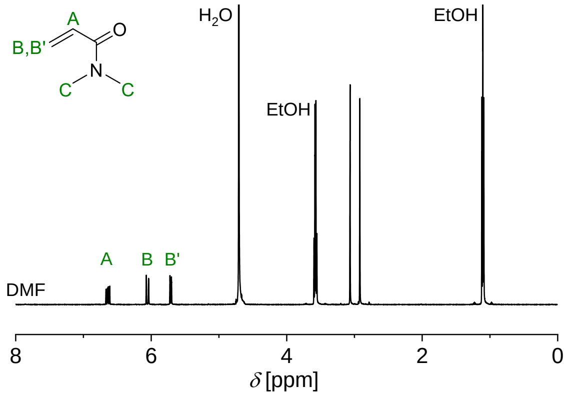

Fig. S 4: Full ^{1}H-NMR spectrum (in D_2O) of the reaction solution of the blue light-induced iniferter RAFT polymerization of DMA in the water-ethanol mixtures (50:50 *w/w*) (20% *w/w*).

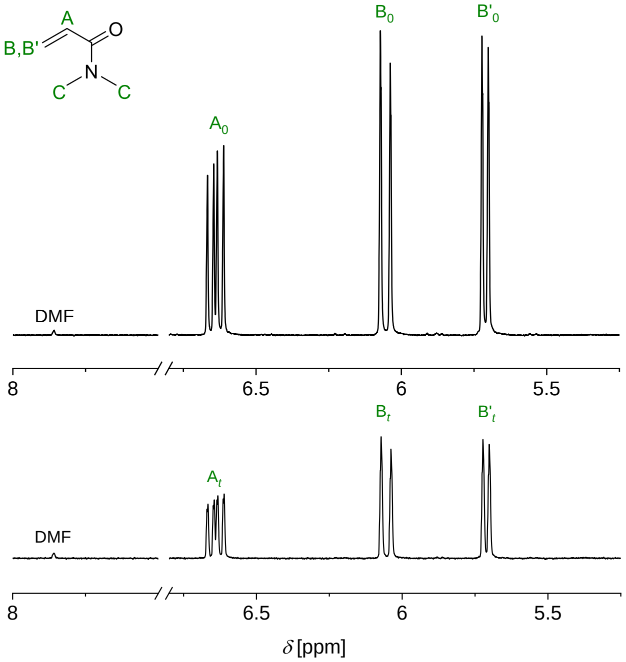

Fig. S 5: ^{1}H-NMR spectrum (in D_2O) of the reaction solution of the photo-iniferter RAFT polymerization of DMA at the start of the polymerization (top) and at the end of the polymerization (bottom). The protons for the determination of the conversion are assigned to the respective signals.

The monomer conversion *p* of DMA after normalization to the DMF signal integral is calculated as follows:

$$p_{\mathrm{DMA}} = 1 - \frac{\mathrm{I}_{\mathrm{A}_t} + \mathrm{I}_{\mathrm{B}_t} + \mathrm{I}_{\mathrm{B'}_t}}{\mathrm{I}_{\mathrm{A}_0} + \mathrm{I}_{\mathrm{B}_0} + \mathrm{I}_{\mathrm{B'}_0}} \tag{1}$$

The theoretical molecular weight of the PDMA macroCTAs was calculated in the following way:

$$\overline{M}_{\mathrm{n,th}} = \frac{[\mathrm{DMA}]_0}{[\mathrm{DDMAT}]_0} \cdot p_{\mathrm{DMA}} \cdot M_{\mathrm{DMA}} + M_{\mathrm{DDMAT}} \tag{2}$$

4.2 Determination of the DMAEA conversion

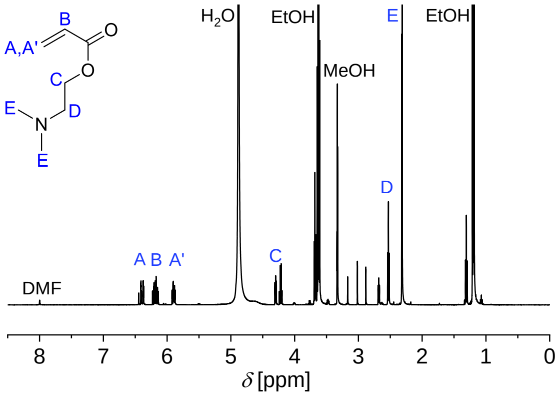

Fig. S 6: Full ^{1}H-NMR spectrum (in MeOH-d_4) of the reaction solution of the blue light-induced iniferter RAFT polymerization of DMAEA in the water-ethanol mixtures (50:50 *w*/*w*) (20% *w*/*w*).

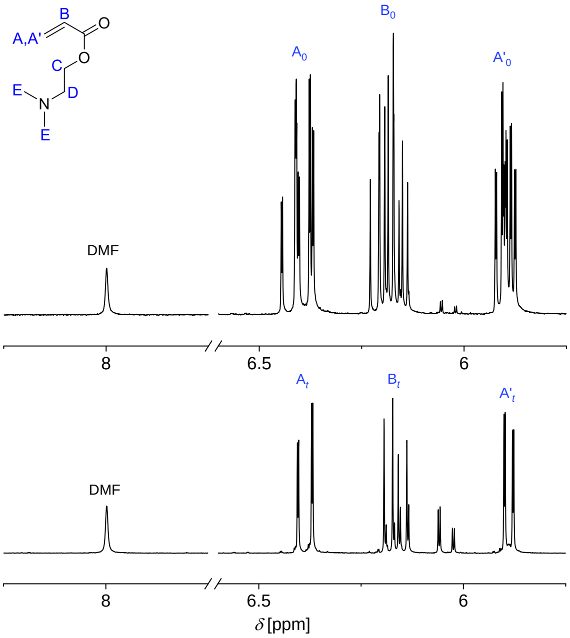

Fig. S 7: ^{1}H-NMR spectrum (in MeOH-d_4) of the reaction solution of the photo-iniferter RAFT polymerization of DMAEA at the start of the polymerization (top) and at the end of the polymerization (bottom). The protons for the determination of the conversion are assigned to the respective signals.

The monomer conversion *p* of DMAEA after normalization to the DMF signal integral is calculated as follows:

$$p_{\mathrm{DMAEA}} = 1 - \frac{\mathrm{I}_{\mathrm{A}_t} + \mathrm{I}_{\mathrm{B}_t} + \mathrm{I}_{\mathrm{A'}_t}}{\mathrm{I}_{\mathrm{A}_0} + \mathrm{I}_{\mathrm{B}_0} + \mathrm{I}_{\mathrm{A'}_0}} \tag{3}$$

The theoretical molecular weight of the PDMAEA macroCTAs was calculated in the following way:

$$\overline{M}_{\mathrm{n,th}} = \frac{[\mathrm{DMAEA}]_0}{[\mathrm{DDMAT}]_0} \cdot p_{\mathrm{DMAEA}} \cdot M_{\mathrm{DMAEA}} + M_{\mathrm{DDMAT}} \tag{4}$$

4.3 Determination of the 4VP conversion

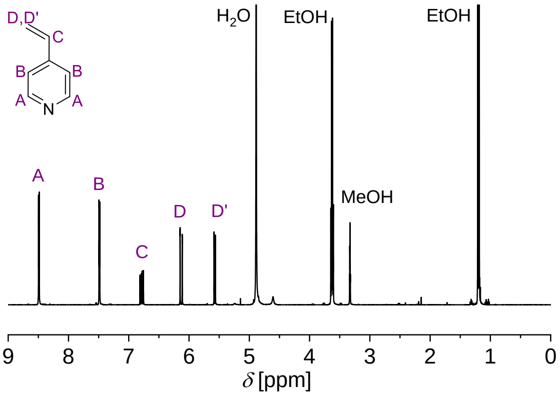

Fig. S 8: Full ^{1}H-NMR spectrum (in MeOH-d_4) of the reaction solution of the blue light-induced iniferter RAFT polymerization of 4VP in the water-ethanol mixtures (50:50 *w*/*w*) (20% *w*/*w*).

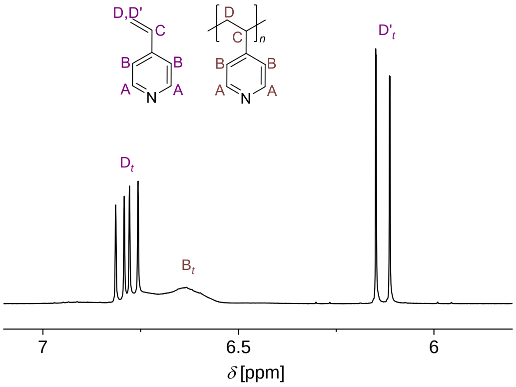

Fig. S 9: ^{1}H-NMR spectrum (MeOH-d_4) of the reaction solution of the photo-iniferter RAFT polymerization of 4VP at the end of the polymerization. The protons for the determination of the conversion are assigned to the respective signals.

The monomer conversion *p* of 4VP is calculated as follows:

$$p_{4\mathrm{VP}} = \frac{\mathrm{I}_{\mathrm{D}_t+\mathrm{B}_t} - \mathrm{I}_{\mathrm{D'}_t}}{\mathrm{I}_{\mathrm{D'}_t} + \mathrm{I}_{\mathrm{D}_t+\mathrm{B}_t}} \qquad (5)$$

The theoretical molecular weight of the P4VP macroCTAs was calculated in the following way:

$$\overline{M}_{\mathrm{n,th}} = \frac{[\mathrm{4VP}]_0}{[\mathrm{DDMAT}]_0} \cdot p_{4\mathrm{VP}} \cdot M_{4\mathrm{VP}} + M_{\mathrm{DDMAT}} \qquad (6)$$

4.4 Determination of the 2VP conversion

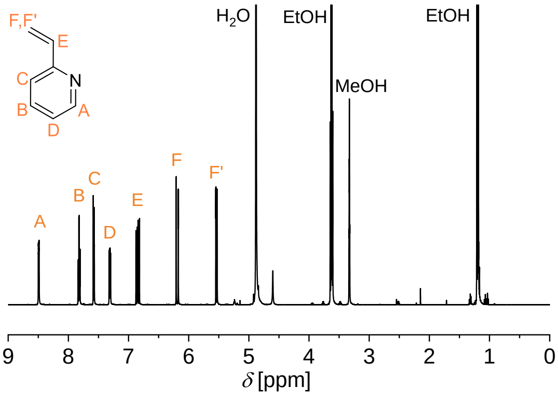

Fig. S 10: Full ^{1}H-NMR spectrum (in MeOH-d_4) of the reaction solution of the blue light-induced iniferter RAFT polymerization of 2VP in the water-ethanol mixtures (50:50 *w*/*w*) (30% *w*/*w*).

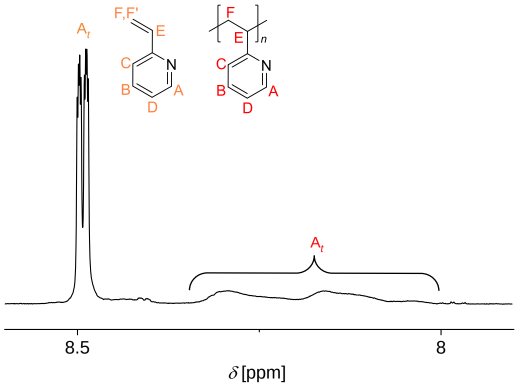

Fig. S 11: ^{1}H-NMR spectrum (in MeOH-d_4) of the reaction solution of the photo-iniferter RAFT polymerization of 2VP at the end of the polymerization. The protons for the determination of the conversion are assigned to the respective signals.

The monomer conversion *p* of 2VP is calculated as follows:

$$p_{\mathrm{2VP}} = \frac{\mathrm{I}_{A_t}}{\mathrm{I}_{A_t + A_t}} \tag{7}$$

The theoretical molecular weight of the P2VP macroCTAs was calculated in the following way:

$$\bar{M}_{\mathrm{n,th}} = \frac{[\mathrm{2VP}]_0}{[\mathrm{DDMAT}]_0} \cdot p_{\mathrm{2VP}} \cdot M_{\mathrm{2VP}} + M_{\mathrm{DDMAT}} \tag{8}$$

5. PDMA homopolymers

5.1 In 20 mL vessels

Table S 1: Synthesized PDMA homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[DMA]_0/[DDMAT]_0 = 500$ in water-ethanol mixtures (50:50 *w/w*) (20% *w/w*).

T [°C]	I_{light} [mW·cm^{-2}]	Sample code [a]	time [min]	conversion [%] [b]	$\overline{M}_{\text{n,th}}$ [kDa] [c]	$\overline{M}_{\text{n,app}}$ [kDa] [d]	$Đ$ [e]
40	16	PDMA$^{1.5}$	31	2.4	1.5	2.4	1.41
		PDMA$^{5.4}$	61	10.2	5.4	4.7	1.36
		PDMA$^{11.6}$	120	22.8	11.6	11.2	1.24
		PDMA$^{24.8}$	240	49.9	24.8	23.1	1.12
40	30	PDMA$^{5.3}$	15	10.1	5.3	4.8	1.39
		PDMA$^{11.8}$	32	23.3	11.8	10.8	1.20
		PDMA$^{21.6}$	62	43.2	21.6	19.7	1.15
		PDMA$^{30.8}$	90	62.5	30.8	28.0	1.12
		PDMA$^{32.8}$	120	66.2	32.8	28.5	1.14
		PDMA$^{42.1}$	240	85.2	42.1	33.2	1.20
40	49	PDMA$^{8.9}$	16	17.5	8.9	9.9	1.22
		PDMA$^{17.1}$	32	34.1	17.1	17.0	1.15
		PDMA$^{27.2}$	63	54.8	27.2	25.1	1.14
		PDMA$^{28.5}$	75	57.4	28.5	22.2	1.21
		PDMA$^{28.7}$	75	58.0	28.7	25.0	1.16
		PDMA$^{29.8}$	80	59.5	29.8	27.0	1.09
		PDMA$^{37.7}$	123	76.3	37.7	32.3	1.16
		PDMA$^{44.8}$	241	90.7	44.8	36.5	1.19

[a] superscripts denote the theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. [b] determined via ^{1}H-NMR spectroscopy. [c] theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. [d] apparent number-averaged molecular weight determined by SEC with PS calibration. [e] dispersity determined by SEC with PS calibration.

Table S 2: Synthesized PDMA homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[DMA]_0/[DDMAT]_0 = 800$ in water-ethanol mixtures (50:50 *w/w*) (20% *w/w*).

T [°C]	I_{light} [mW·cm^{-2}]	Sample code [a]	time [min]	conversion [%] [b]	$\overline{M}_{\text{n,th}}$ [kDa] [c]	$\overline{M}_{\text{n,app}}$ [kDa] [d]	$Đ$ [e]
40	49	PDMA$^{31.5}$	60	39.9	31.5	26.2	1.16
		PDMA$^{33.8}$	60	42.1	33.8	35.9	1.12
		PDMA$^{37.2}$	75	46.3	37.2	32.2	1.13
		PDMA$^{43.0}$	90	52.7	43.0	36.8	1.15

[a] superscripts denote the theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. [b] determined via ^{1}H-NMR spectroscopy. [c] theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. [d] apparent number-averaged molecular weight determined by SEC with PS calibration. [e] dispersity determined by SEC with PS calibration.

5.2 In 250 mL vessels

Table S 3: Synthesized PDMA homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[DMA]_0/[DDMAT]_0 = 500$ in water-ethanol mixtures (50:50 *w/w*) (20% *w/w*).

T [°C]	I_{light} [mW·cm^{-2}]	Sample code [a]	time [min]	conversion [%] [b]	$\overline{M}_{\text{n,th}}$ [kDa] [c]	$\overline{M}_{\text{n,app}}$ [kDa] [d]	$Đ$ [e]
40	52	PDMA$^{2.7}$	15	4.7	2.7	4.8	1.25
		PDMA$^{9.8}$	30	18.8	9.8	9.6	1.20
		PDMA$^{17.1}$	30	24.2	12.5	7.9	1.20
		PDMA$^{20.0}$	60	39.2	20.0	18.6	1.15
		PDMA$^{25.5}$	64	50.1	25.5	17.2	1.12
		PDMA$^{23.5}$	70	46.1	23.5	17.8	1.16
		PDMA$^{23.7}$	70	46.5	23.7	19.1	1.17
		PDMA$^{31.1}$	120	61.3	31.1	29.4	1.08
		PDMA$^{32.9}$	120	64.9	32.9	28.5	1.12
		PDMA$^{43.0}$	240	84.9	43.0	37.3	1.10

T [°C]	I_{light} [mW·cm^{-2}]	Sample code a)	time [min]	conversion [%] b)	$\bar{M}_{n,th}$ [kDa] c)	$\bar{M}_{n,app}$ [kDa] d)	$Đ$ e)
		PDMA$^{40.6}$	241	80.2	40.6	36.0	1.08

a) superscripts denote the theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. b) determined via ^{1}H-NMR spectroscopy. c) theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. d) apparent number-averaged molecular weight determined by SEC with PS calibration. e) dispersity determined by SEC with PS calibration.

5.3 In 500 mL vessels

Table S 4: Synthesized PDMA homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[DMA]_0/[DDMAT]_0 = 500$ in water-ethanol mixtures (50:50 *w*/*w*) (20% *w*/*w*).

T [°C]	I_{light} [mW·cm^{-2}]	Sample code a)	time [min]	conversion [%] b)	$\bar{M}_{n,th}$ [kDa] c)	$\bar{M}_{n,app}$ [kDa] d)	$Đ$ e)
40	55	PDMA$^{4.4}$	22	8.1	4.4	5.7	1.30
		PDMA$^{13.9}$	60	27.1	13.9	14.8	1.19
		PDMA$^{29.4}$	120	58.1	29.4	25.2	1.14
		PDMA$^{43.0}$	240	78.6	39.6	34.4	1.12

a) superscripts denote the theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. b) determined via ^{1}H-NMR spectroscopy. c) theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. d) apparent number-averaged molecular weight determined by SEC with PS calibration. e) dispersity determined by SEC with PS calibration.

6. PDMAEA homopolymers

6.1 In 20 mL vessels

Table S 5: Synthesized PDMAEA homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[DMAEA]_0/[DDMAT]_0 = 320$ in water-ethanol mixtures (50:50 *w*/*w*) (20% *w*/*w*).

T [°C]	I_{light} [mW·cm^{-2}]	Sample code a)	time [min]	conversion [%] b)	$\overline{M}_{n,th}$ [kDa] c)	$\overline{M}_{n,app}$ [kDa] d)	$Đ$ e)
40	49	PDMAEA$^{4.7}$	16	8.9	4.7	3.2	1.25
		PDMAEA$^{8.4}$	31	16.5	8.4	5.3	1.23
		PDMAEA$^{13.6}$	61	27.0	13.6	8.2	1.20
		PDMAEA$^{21.4}$	120	43.0	21.4	13.6	1.15
		PDMAEA$^{30.8}$	240	62.2	30.8	17.7	1.23

a) superscripts denote the theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. b) determined via ^{1}H-NMR spectroscopy. c) theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. d) apparent number-averaged molecular weight determined by SEC with PS calibration. e) dispersity determined by SEC with PS calibration.

Table S 6: Synthesized PDMAEA homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[DMAEA]_0/[DDMAT]_0 = 500$ in water-ethanol mixtures (50:50 *w*/*w*) (20% *w*/*w*).

T [°C]	I_{light} [mW·cm^{-2}]	Sample code a)	time [min]	conversion [%] b)	$\overline{M}_{n,th}$ [kDa] c)	$\overline{M}_{n,app}$ [kDa] d)	$Đ$ e)
40	49	PDMAEA$^{5.6}$	15	8.9	7.1	6.8	1.27
		PDMAEA$^{8.1}$	17	10.8	8.1	5.0	1.23
		PDMAEA$^{12.2}$	30	16.5	12.2	6.1	1.37
		PDMAEA$^{14.7}$	30	19.1	14.7	11.7	1.21
		PDMAEA$^{21.5}$	60	29.4	21.5	9.4	1.43
		PDMAEA$^{24.1}$	60	31.6	24.1	15.0	1.35
		PDMAEA$^{33.4}$	120	46.1	33.4	15.9	1.40
		PDMAEA$^{37.6}$	120	49.9	37.6	19.8	1.42
		PDMAEA$^{43.2}$	240	59.8	43.2	21.7	1.41
		PDMAEA$^{46.7}$	243	61.7	46.7	23.0	1.44

a) superscripts denote the theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. b) determined via ^{1}H-NMR spectroscopy. c) theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. d) apparent number-averaged molecular weight determined by SEC with PS calibration. e) dispersity determined by SEC with PS calibration.

6.2 In 250 mL vessels

Table S 7: Synthesized PDMAEA homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[DMAEA]_0/[DDMAT]_0 = 500$ in water-ethanol mixtures (50:50 *w*/*w*) (20% *w*/*w*).

T [°C]	I_{light} [mW·cm^{-2}]	Sample code a)	time [min]	conversion [%] b)	$\overline{M}_{n,th}$ [kDa] c)	$\overline{M}_{n,app}$ [kDa] d)	$Đ$ e)
40	52	PDMAEA$^{5.6}$	15	6.8	5.6	4.8	1.29
		PDMAEA$^{9.0}$	30	11.3	9.0	7.6	1.21
		PDMAEA$^{21.1}$	60	27.0	21.1	11.0	1.26
		PDMAEA$^{30.8}$	120	39.6	30.8	16.3	1.25
		PDMAEA$^{37.6}$	242	48.6	37.6	17.5	1.42

a) superscripts denote the theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. b) determined via ^{1}H-NMR spectroscopy. c) theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. d) apparent number-averaged molecular weight determined by SEC with PS calibration. e) dispersity determined by SEC with PS calibration.

7. P4VP homopolymers

7.1 In 40 mL vessels

Table S 8: Synthesized P4VP homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of [4VP]$_0$/[DDMAT]$_0$ = 470 in water-ethanol mixtures (50:50 *w*/*w*) (20% *w*/*w*).

T [°C]	I_{light} [mW·cm^{-2}]	Sample code [a]	time [min]	conversion [%] [b]	$\bar{M}_{\text{n,th}}$ [kDa] [c]	$\bar{M}_{\text{n,app}}$ [kDa] [d]	*Đ* [e]
40	49	P4VP$^{0.6}$	30	0.6	0.6	2.2	1.25
		P4VP$^{0.7}$	30	0.6	0.7	3.1	1.17
		P4VP$^{5.2}$	58	9.8	5.2	6.5	1.21
		P4VP$^{3.9}$	62	7.2	3.9	5.7	1.19
		P4VP$^{3.5}$	68	6.4	3.5	8.3	1.23
		P4VP$^{8.5}$	120	16.5	8.5	13.9	1.19
		P4VP$^{9.7}$	120	19.3	9.7	12.1	1.18
		P4VP$^{11.4}$	125	22.4	11.4	14.2	1.16
		P4VP$^{18.9}$	240	37.6	18.9	23.9	1.22
		P4VP$^{20.0}$	240	40.6	20.0	22.9	1.25
		P4VP$^{27.5}$	360	56.2	27.5	33.9	1.22
50	49	P4VP$^{2.4}$	30	4.2	2.4	6.2	1.23
		P4VP$^{3.5}$	59	6.3	3.5	12.1	1.19
		P4VP$^{15.2}$	119	30.1	15.2	21.8	1.23
		P4VP$^{25.6}$	240	51.3	25.6	34.5	1.34

[a] superscripts denote the theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. [b] determined via ^{1}H-NMR spectroscopy. [c] theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. [d] apparent number-averaged molecular weight determined by SEC with PS calibration. [e] dispersity determined by SEC with PS calibration.

Table S 9: Synthesized P4VP homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of [4VP]$_0$/[DDMAT]$_0$ = 470 in water-ethanol mixtures (50:50 *w*/*w*) (30% *w*/*w*).

T [°C]	I_{light} [mW·cm^{-2}]	Sample code [a]	time [min]	conversion [%] [b]	$\bar{M}_{\text{n,th}}$ [kDa] [c]	$\bar{M}_{\text{n,app}}$ [kDa] [d]	*Đ* [e]
40	49	P4VP$^{1.3}$	30	1.9	1.3	3.0	1.26
		P4VP$^{5.5}$	60	10.0	5.5	7.6	1.23
		P4VP$^{12.6}$	120	23.8	12.6	15.8	1.18
		P4VP$^{25.1}$	240	48.2	25.1	29.6	1.35
		P4VP$^{33.8}$	360	65.3	33.8	37.8	1.36

[a] superscripts denote the theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. [b] determined via ^{1}H-NMR spectroscopy. [c] theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. [d] apparent number-averaged molecular weight determined by SEC with PS calibration. [e] dispersity determined by SEC with PS calibration.

Table S 10: Synthesized P4VP homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of [4VP]$_0$/[DDMAT]$_0$ = 750 in water-ethanol mixtures (50:50 *w*/*w*) (20% *w*/*w*).

T [°C]	I_{light} [mW·cm^{-2}]	Sample code [a]	time [min]	conversion [%] [b]	$\bar{M}_{\text{n,th}}$ [kDa] [c]	$\bar{M}_{\text{n,app}}$ [kDa] [d]	*Đ* [e]
40	49	P4VP$^{5.7}$	60	6.8	5.7	8.8	1.29
		P4VP$^{4.5}$	65	5.4	4.5	9.7	1.26
		P4VP$^{8.6}$	120	10.7	8.6	16.9	1.22
		P4VP$^{13.3}$	121	16.5	13.3	17.3	1.23
		P4VP$^{20.3}$	240	26.0	20.3	32.6	1.17
		P4VP$^{21.1}$	240	26.5	21.1	29.6	1.26
		P4VP$^{31.6}$	361	39.9	31.6	36.2	1.44

[a] superscripts denote the theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. [b] determined via ^{1}H-NMR spectroscopy. [c] theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. [d] apparent number-averaged molecular weight determined by SEC with PS calibration. [e] dispersity determined by SEC with PS calibration.

7.2 In 250 mL vessels

Table S 11: Synthesized P4VP homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[4VP]_0/[DDMAT]_0 = 470$ in water-ethanol mixtures (50:50 *w*/*w*) (20% *w*/*w*).

T [°C]	I_{light} [mW·cm^{-2}]	Sample code a)	time [min]	conversion [%] b)	$\bar{M}_{n,th}$ [kDa] c)	$\bar{M}_{n,app}$ [kDa] d)	*Đ* e)
40	52	P4VP$^{1.2}$	60	1.7	1.2	3.0	1.23
		P4VP$^{4.9}$	120	9.2	4.9	7.6	1.27
		P4VP$^{12.0}$	241	23.5	12.0	15.9	1.19
		P4VP$^{18.1}$	360	35.8	18.1	22.8	1.21

a) superscripts denote the theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. b) determined via ^{1}H-NMR spectroscopy. c) theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. d) apparent number-averaged molecular weight determined by SEC with PS calibration. e) dispersity determined by SEC with PS calibration.

Table S 12: Synthesized P4VP homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[4VP]_0/[DDMAT]_0 = 470$ in water-ethanol mixtures (50:50 *w*/*w*) (30% *w*/*w*).

T [°C]	I_{light} [mW·cm^{-2}]	Sample code a)	time [min]	conversion [%] b)	$\bar{M}_{n,th}$ [kDa] c)	$\bar{M}_{n,app}$ [kDa] d)	*Đ* e)
40	52	P4VP$^{1.1}$	60	1.4	1.1	2.9	1.27
		P4VP$^{5.0}$	120	9.3	5.0	7.1	1.21
		P4VP$^{13.9}$	243	27.2	13.9	17.6	1.20
		P4VP$^{19.5}$	360	39.1	19.5	22.8	1.13
		P4VP$^{21.5}$	360	42.5	21.5	25.7	1.24
40	86	P4VP$^{2.1}$	60	3.4	2.1	5.1	1.22
		P4VP$^{7.3}$	120	13.8	7.3	12.1	1.14
		P4VP$^{16.7}$	240	32.6	16.7	23.8	1.25
		P4VP$^{25.0}$	360	49.1	25.0	35.9	1.23
50	526	P4VP$^{2.1}$	61	3.5	2.1	4.6	1.29
		P4VP$^{7.3}$	120	13.6	7.1	11.2	1.17
		P4VP$^{16.7}$	241	31.6	16.1	24.9	1.12
		P4VP$^{25.0}$	360	46.9	23.7	37.1	1.11

a) superscripts denote the theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. b) determined via ^{1}H-NMR spectroscopy. c) theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. d) apparent number-averaged molecular weight determined by SEC with PS calibration. e) dispersity determined by SEC with PS calibration.

Table S 13: Synthesized P4VP homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[4VP]_0/[DDMAT]_0 = 760$ in water-ethanol mixtures (50:50 *w*/*w*) (30% *w*/*w*).

T [°C]	I_{light} [mW·cm^{-2}]	Sample code a)	time [min]	conversion [%] b)	$\bar{M}_{n,th}$ [kDa] c)	$\bar{M}_{n,app}$ [kDa] d)	*Đ* e)
40	86	P4VP$^{2.7}$	60	3.0	2.7	60	1.31
		P4VP$^{5.6}$	120	6.6	5.6	6.8	1.18
		P4VP$^{22.5}$	240	27.9	22.5	37.5	1.08
		P4VP$^{33.1}$	360	41.2	33.1	55.4	1.07
		P4VP$^{42.2}$	480	52.7	42.2	73.1	1.22

8. P2VP homopolymers

8.1 In 40 mL vessels

Table S 14: Synthesized P2VP homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[2VP]_0/[DDMAT]_0 = 470$ in water-ethanol mixtures (50:50 *w*/*w*) (30% *w*/*w*).

T [°C]	I_{light} [mW·cm^{-2}]	Sample code a)	time [min]	conversion [%] b)	$\bar{M}_{\mathrm{n,th}}$ [kDa] c)	$\bar{M}_{\mathrm{n,app}}$ [kDa] d)	$Đ$ e)
40	49	P2VP$^{2.5}$	60	4.2	2.5	2.7	1.33
		P2VP$^{4.7}$	120	8.7	4.7	6.7	1.27
		P2VP$^{11.0}$	240	21.3	11.0	16.6	1.19
		P2VP$^{17.8}$	360	34.9	17.8	26.6	1.17
50	49	P2VP$^{1.1}$	31	1.6	1.1		
		P2VP$^{3.4}$	62	6.1	3.4	5.1	1.24
		P2VP$^{7.2}$	120	13.8	7.2	11.7	1.28
		P2VP$^{17.0}$	240	33.6	17.0	27.3	1.21
		P2VP$^{23.2}$	360	46.1	23.2	42.1	1.14
60	49	P2VP$^{1.0}$	29	1.4	1.0		
		P2VP$^{2.5}$	60	4.3	2.5	4.3	1.36
		P2VP$^{8.6}$	120	16.5	8.6	13.7	1.21
		P2VP$^{18.7}$	240	37.1	18.7	33.6	1.23
		P2VP$^{25.7}$	360	51.1	25.7	54.3	1.09
70	49	P2VP$^{2.1}$	32	3.6	2.1		
		P2VP$^{4.2}$	60	7.7	4.2	7.1	1.17
		P2VP$^{11.9}$	119	23.2	11.9	17.7	1.21
		P2VP$^{22.0}$	241	43.6	22.0	45.6	1.12
		P2VP$^{29.0}$	360	57.9	29.0	73.7	1.10

a) superscripts denote the theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. b) determined via ^{1}H-NMR spectroscopy. c) theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. d) apparent number-averaged molecular weight determined by SEC with PS calibration. e) dispersity determined by SEC with PS calibration.

8.2 In 250 mL vessels

Table S 15: Synthesized P2VP homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[2VP]_0/[DDMAT]_0 = 470$ in water-ethanol mixtures (50:50 *w*/*w*) (30% *w*/*w*).

T [°C]	I_{light} [mW·cm^{-2}]	Sample code a)	time [min]	conversion [%] b)	$\bar{M}_{\mathrm{n,th}}$ [kDa] c)	$\bar{M}_{\mathrm{n,app}}$ [kDa] d)	$Đ$ e)
60	52	P2VP$^{1.6}$	60	2.5	1.6	2.2	1.26
		P2VP$^{4.9}$	120	9.1	4.9	6.7	1.25
		P2VP$^{13.6}$	240	26.9	13.6	19.6	1.19
		P2VP$^{20.6}$	360	41.1	20.6	33.0	1.17
70	52	P2VP$^{3.1}$	63	5.6	3.1	4.3	1.35
		P2VP$^{8.4}$	119	16.3	8.4	11.5	1.25
		P2VP$^{18.1}$	242	36.1	18.1	30.4	1.17
		P2VP$^{25.4}$	360	50.7	25.4	50.0	1.14

a) superscripts denote the theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. b) determined via ^{1}H-NMR spectroscopy. c) theoretical number-average molecular weight determined by ^{1}H-NMR spectroscopy. d) apparent number-averaged molecular weight determined by SEC with PS calibration. e) dispersity determined by SEC with PS calibration.

9. Determination of required energy for the polymer synthesis

In order to estimate the required energy to perform light-induced iniferter RAFT polymerization at different temperatures some assumptions are made. These assumptions were implemented to determine and compare the energy consumption between the experiments at 40 °C and 70 °C. Due to the fact that the polymerization vessel is immersed in a stirred heat bath, there is a temperature equilibrium between the polymerization solution and the surrounding heat bath. Since the polymer and monomer concentration change with time and not all the required parameters for water/ethanol mixtures are available, therefore, only water (as reaction medium) and the water bath are considered as a model system. In this study, all polymerizations were carried out in a 300 mL water bath and half of the amount of solvent used for the polymerization was water as well. Therefore, it is assumed that a polymerization system including 500 mL water in a 600 mL beaker is on top of a hot plate as a heating source. Heater is required for heating of the water to raise the temperature as well as carrying out the polymerization at a constant temperature in a given period of time.

Due to the heat transfer to the surrounding environment, the energy is consumed to keep the temperature constant (non-isothermal system). The heat is transferred out of the beaker on the one hand through the glass wall and on the other hand through direct contact with air. To keep the temperature constant, the heat loss must be compensated by heating of the plate. Due to this, the net heat transferred into or out of the system consists of two contributions: 1) the heating of the water to the desired temperature ($\Delta Q_{\text{heating-up}}$), and 2) the heating of the water to hold it at a constant temperature in a given time period. The latest term can be estimated using the heat loss through the glass wall (ΔQ_{glass}), and the heat loss through the direct contact of the water surface with the air (ΔQ_{air}) (see Fig. S 11). Other influencing factors for the determination of the energy such as the heat of reaction generated over time and the heat generated by the blue LED were neglected (the aluminum cylinder dissipates most of the heat from the LED lamp). As well, the evaporation of solvent is not considered. All formulas for the calculation as well as material-specific characteristic data were taken from the VDI Heat Atlas.[1]

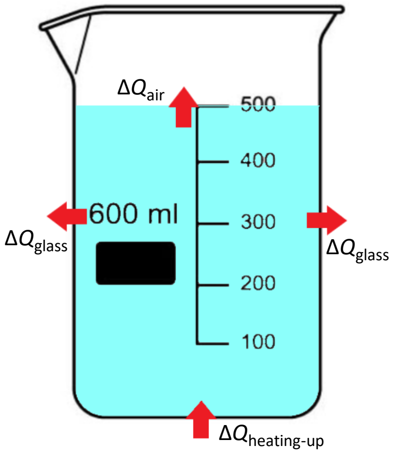

Fig. S 12: Schematic representation of the heat transfer from the model system.

The required energy $\Delta Q_{\text{heating-up}}$ for the heating-up of the water depends on the mass *m*, the heat capacity c_p and the difference in temperature ΔT and is calculated *via*

$$\Delta Q_{\text{heating-up}} = m \cdot c_p \cdot \Delta T \qquad (9)$$

Part of the heat transferred by time from water to surrounding air through the glass wall was determined based on the calculation described in the chapter “Fundamentals of calculation methods for heat conduction, convective heat transfer and thermal radiation” using the example of heat transfer through a plane wall.[1] The heat flow is determined by the heat transmission coefficient k, the lateral surface of the beaker A and the difference in temperature ΔT.

$$\dot{Q}_{\text{glass}} = k \cdot A \cdot \Delta T \tag{10}$$

The heat transmission coefficient k is calculated using the heat transfer coefficient of the water bath α_1, the thickness of the wall Δw, the heat conductivity coefficient of glass λ_w and the heat transfer coefficient of the surrounding air α_2.

$$k = \frac{1}{\frac{1}{\alpha_1}+\frac{\Delta w}{\lambda_w}+\frac{1}{\alpha_2}} \tag{11}$$

To determine the heat transfer coefficient α_1 according to equations from the chapter “heat transfer and power consumption in stirred vessels”,[1] the Nusselt number Nu for a beam stirrer was calculated *via* the following equation with the constant C, the Reynolds number Re, the Prandtl number Pr and the dynamic viscosity η in which the viscosity term is negligible.

$$Nu = \mathrm{C} \cdot Re^{\frac{2}{3}} \cdot Pr^{\frac{1}{3}} \cdot \left(\frac{\eta}{\eta_w}\right)^{0.14} \tag{12}$$

In order to calculate the constant C, the following equation for a vessel with a blade stirrer and without current breaker is used. In this equation, d stands for diameter and h for height.

$$\mathrm{C} = 0.6 \cdot \left(\frac{d_{\text{stirrer}}}{d_{\text{vessel}}}\right)^{-0.25} \cdot \left(\frac{h_{\text{liquid}}}{d_{\text{vessel}}}\right)^{0.15} \cdot \left(\frac{h_{\text{stirrer}}}{h_{\text{fill height}}}\right)^{0.15} \tag{13}$$

The Reynolds number Re from equation 12 was calculated by

$$\mathrm{Re} = \frac{n \cdot d_{\text{stirrer}}{}^{2} \cdot \rho}{\eta} \tag{14}$$

Subsequently the heat transfer coefficient α_1 was determined by

$$\alpha = \frac{Nu \cdot \lambda}{d_v} \tag{15}$$

where, λ is the conductivity coefficient and d_v denotes the vessel diameter.

For the determination of α_2, a heat coefficient of 10 W/(m^2·K) is supposed to use for the determination of ΔQ_{wall} and ΔQ_{air} (typical value for a low speed flow of air over a surface).

The heat exchange between the free surface of the water and the ambient air circulating over the surface occurs mainly *via* convection. According to the chapter “Heat Transfer in Free Convection: Fundamentals”, the heat flow $\dot{Q}_{\text{air}}$ was calculated *via*

$$\dot{Q}_{\mathrm{air}} = \alpha_2 \cdot A \cdot \Delta T \quad (16)$$

In order to determine the thermal energy change $\Delta Q_{\mathrm{glass}}$ and ΔQ_{air}, the heat flow $\dot{Q}_{\mathrm{glass}}$ as well as $\dot{Q}_{\mathrm{air}}$ are multiplied by the duration time of the reaction. For the same 2VP conversion of 50 %, based on the kinetic data, the reaction time of 12 h and 6 h were respectively determined for the reaction temperature of 40 °C and 70 °C.

The required power P of the blue LED lamp for the polymerization was determined by experimental data of the voltage V and current I followed by equation 17.

$$P = V \cdot I \quad (17)$$

The energy ΔE_{LED} is determined by multiplication of the power P with the reaction time.

References

1 P. Stephan, S. Kabelac, M. Kind, D. Mewes, K. Schaber and T. Wetzel, eds., *VDI-Wärmeatlas.* Springer Vieweg, Berlin, Heidelberg, 12th edn., 2019.