

In Situ EPR and Raman Spectroscopy in the Curing of Bis-Methacrylate-Styrene resins

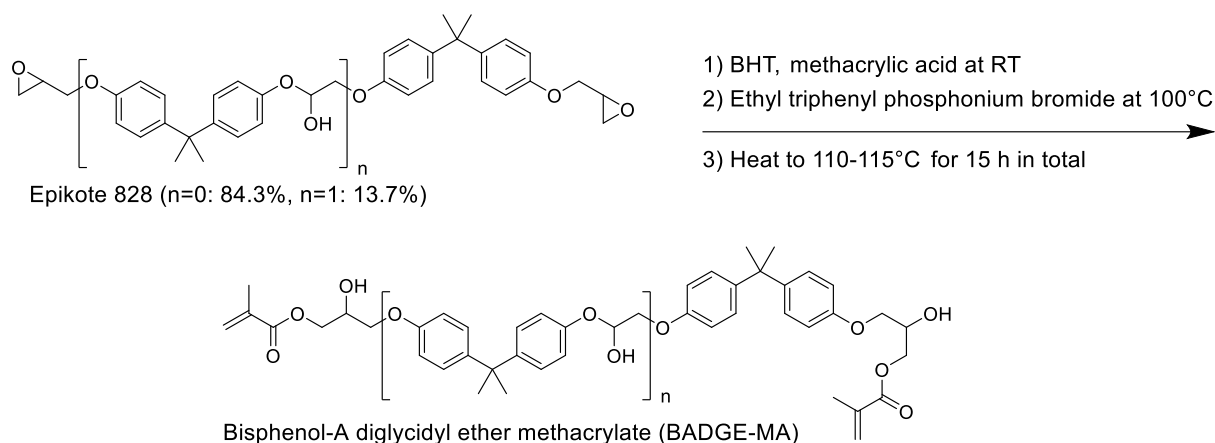
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Synthesis of BADGE-MA

A 3 l three-necked round bottom flask was equipped with mechanical stirrer, thermocouple and reflux condenser, to which 1376.32 g (3.68 mol) Epikote 828, 623.68 g (7.24 mol) methacrylic acid, and 2 g butylated hydroxy toluene (BHT) (9 mmol) were added. The mixture was purged with air for 30 min at room temperature followed by heating to 100 °C and addition of 1.4 g ethyl triphenyl phosphonium bromide (4 mmol). The mixture was heated to 110 °C and the reaction was monitored through its acid value according to ISO standard ISO02114. After 7 h the acid value had decreased to 47.7 mg KOH/g and the mixture was cooled to room temperature and left overnight. The mixture was heated in 60 min to 115 °C. After 10 h of total reaction time the acid and epoxy value were determined and 67 g of Epikote 828 was added to the mixture to make up for the difference in the measured acid and epoxy value. After 8 h the mixture was cooled to room temperature and left overnight. On day 3 the viscous mixture was heated slowly to 115 °C, with stirring possible only after reaching 66 °C. When an acid value of 7.9 was reached the mixture was cooled and poured into 100 ml containers and stored at 7 °C until use. The final acid and epoxy values are 6.57 and 10.7 mg KOH/g, resp. ¹H-NMR spectroscopy was used to confirm the presence of the vinyl groups.



Scheme S 1: Synthesis of BADGE-MA.

Acid numbers were determined according to ISO2114, however the toluene/ethanol (1:1) solvent mixture was replaced by a xylene (mixture of isomer)/ethanol (1:1) mix. The epoxy number was determined according to ISO3001. Epikote 828 is a commercially available glycidyl ether of bisphenol A, which has an initial epoxy value of 292 mg KOH/g.

Characterization of BADGE-MA

¹H-NMR spectroscopy

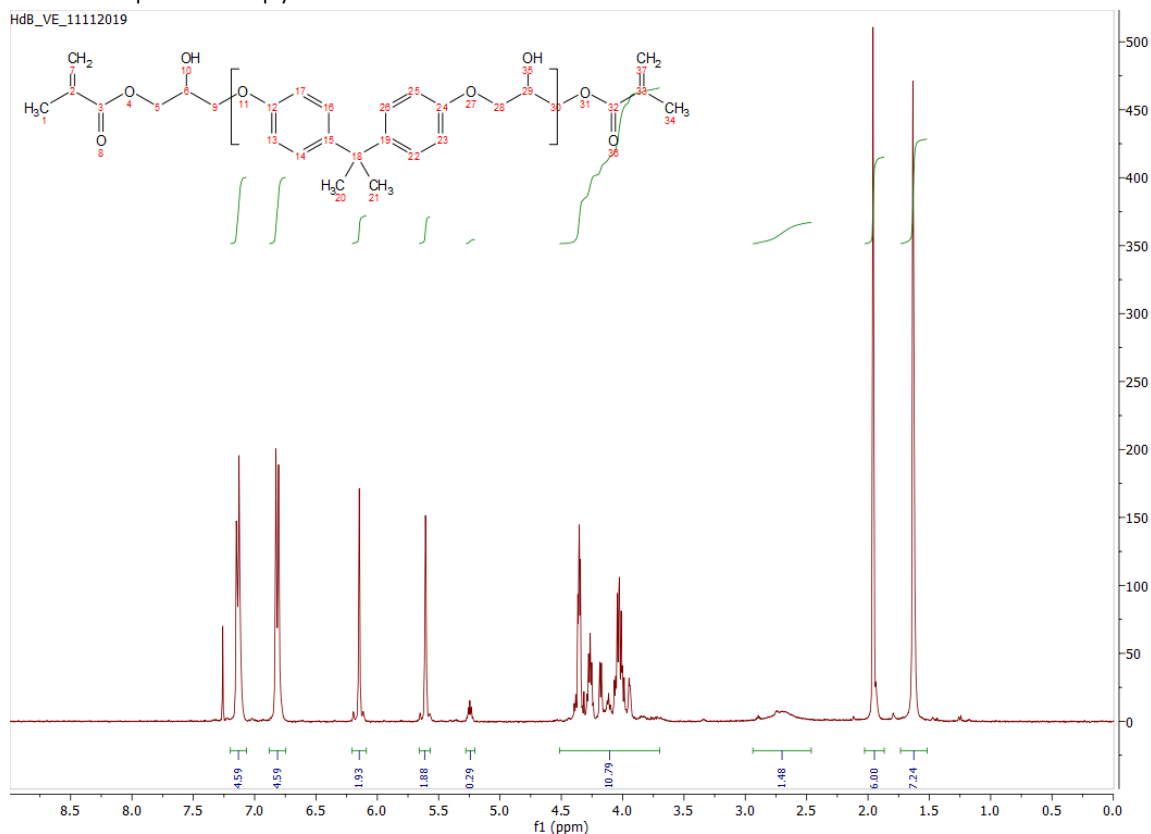


Figure S 1; ¹H-NMR of BADGE-MA in CDCl₃.

The number of repeat units in the methacrylate ester (BADGE-MA) was determined by ¹H-NMR spectroscopy (Figure S 1). ¹H-NMR (400 MHz, Chloroform-*d*) δ 7.19 – 7.07 (m, 5H), 6.82 (d, *J* = 8.5 Hz, 5H), 6.15 (s, 2H), 5.61 (s, 2H), 4.58 – 3.61 (m, 10H), 2.79 (s, 2H), 1.96 (s, 6H), 1.63 (s, 7H).

The ratio of the integral of the -CH₃ singlets at 1.96 and 1.63 was used to determine the number of repeat units, which gives *n* = 1.2. Alternatively, the ratio between the sum of the area of the aromatic protons at 7.19-7.07 and 6.82 ppm and vinylic protons at 6.15 and 5.61 ppm can be used. $((4.59+4.59)/8)/((1.93+1.88)/4) = 1.20$.

Size exclusion chromatography

Gel Permeation Chromatography (GPC) was performed on a Hewlett & Packard 1100 system equipped with three PL-gel 3 μm MIXED-E columns in series. The columns were operated at 40 °C using THF as eluent with a flow rate of 1 ml/min. A GBC LC 1240 RI detector was used at 35°C. The system was calibrated on polystyrene standards. 10 mg of VE was dissolved in 2 ml of THF in a GC vial. To this was added 5-10 μl toluene as internal standard and the solution was passed through a 0.20 μm PTFE syringe filter.

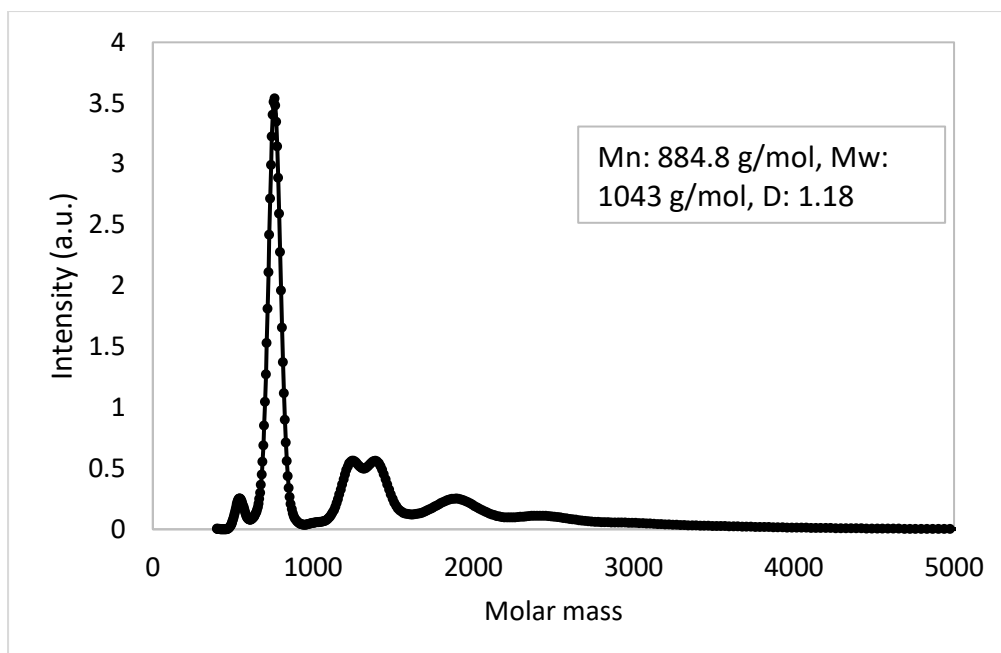


Figure S 2: GPC trace of BADGE-MA.

GPC has only limited use in determining the molar mass of the BADGE-MA as several factors can affect the retention time on the column, unless the calibration is made specifically for the compound measured. The molar mass determined is therefore an indication only. GPC shows that there are oligomers of several chain lengths (Figure S 2). The dispersity of the compound/oligomer, $D = 1.2$, determined corresponds well with the distribution calculated from $^1\text{H-NMR}$ and FT-IR spectroscopy.

FT-IR spectroscopy

A drop of BADGE-MA dissolved in acetonitrile was deposited on ATR crystal of an ATR-FTIR spectrometer (Figure S 3). A calibration curve was prepared using a series of mol ratio mixtures of the model compounds 4,4'-(propane-2,2-diyl)bis(ethoxybenzene) and 2-hydroxyethyl methacrylate (HEMA) dissolved in acetonitrile (Figure S 4). The diethyl ether of BPA was synthesized as reported below. BPA ($\geq 99.0\%$) and HEMA ($\geq 99.0\%$) were obtained from SigmaAldrich and used as received. The ratio of the areas of the C-O stretch absorption band at 1244 cm^{-1} and the carbonyl band at 1715 cm^{-1} of a VE solution in acetonitrile allowed for the 'n'-value to be determined to be 1.2 by interpolation.

4,4'-(propane-2,2-diyl)bis(ethoxybenzene)¹ 20 ml DMF was added to Bisphenol A (2.28 g, 10 mmol) and potassium carbonate (3.48 g, 25 mmol) in a round bottomed flask. Ethyl bromide (1.87 ml, 2.72 g, 25 mmol) was added at room temperature to the stirred mixture. After 16 h the reaction mixture was poured into distilled water and extracted three times with DCM. The extract was washed with water, dried over Na_2SO_4 and the solvent was removed *in vacuo*. The product was recrystallized from ethanol/water (3:1) and yielded a white crystalline solid (0.87 g, 30%)

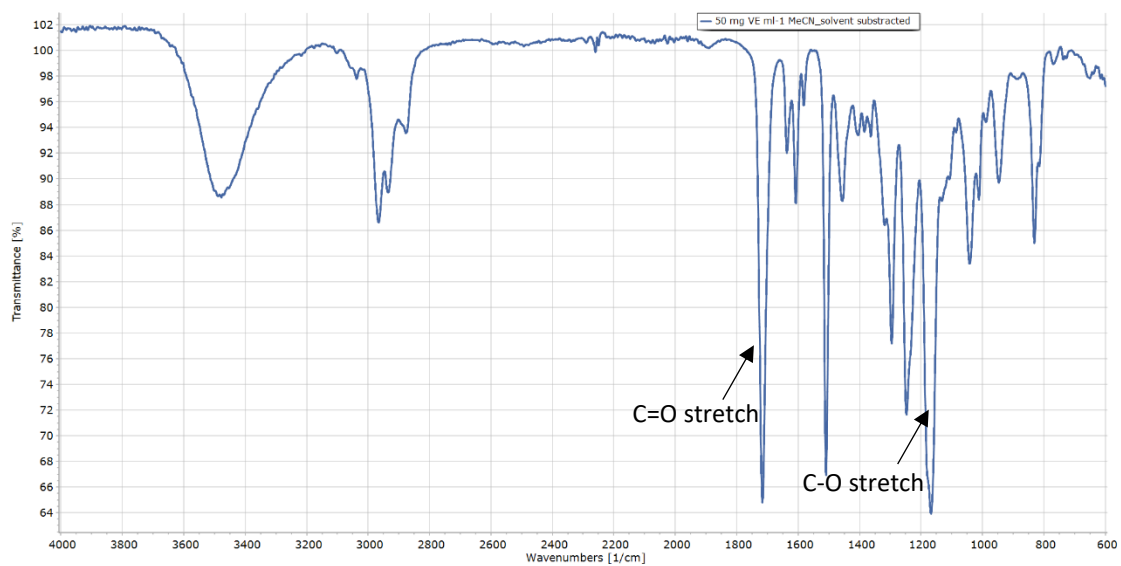


Figure S 3: FT-IR spectrum of BADGE-MA recorded from a solution of 50 mg/mL in MeCN drop cast on the ATR crystal. Solvent subtracted.

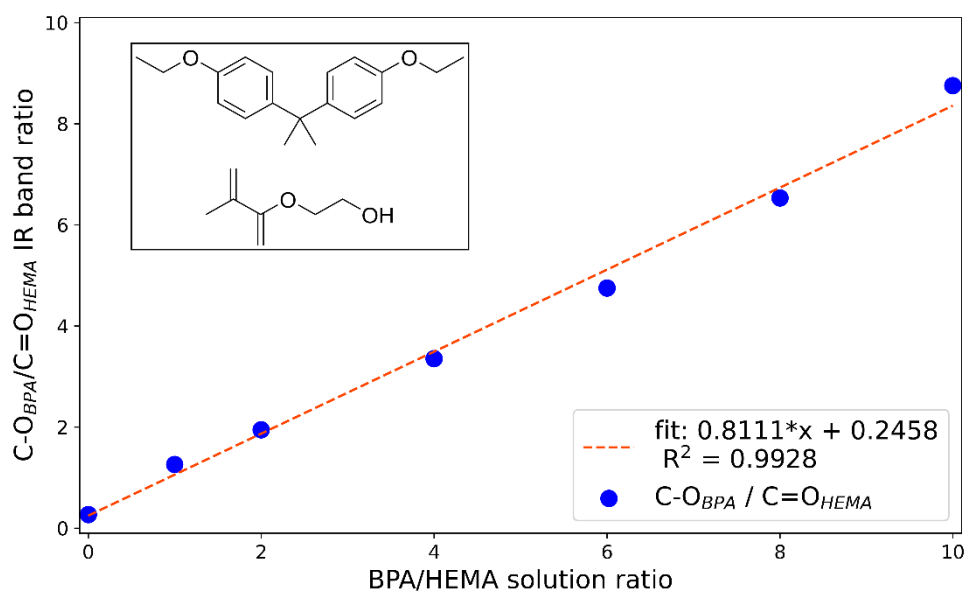


Figure S 4: Calibration curve prepared from solutions with various ratios of the diethyl ether of BPA and HEMA. Recorded with ATR-FT-IR spectroscopy and used to determine number of repeating units in BADGE-MA.

Curing of Resins with Manganese Soaps

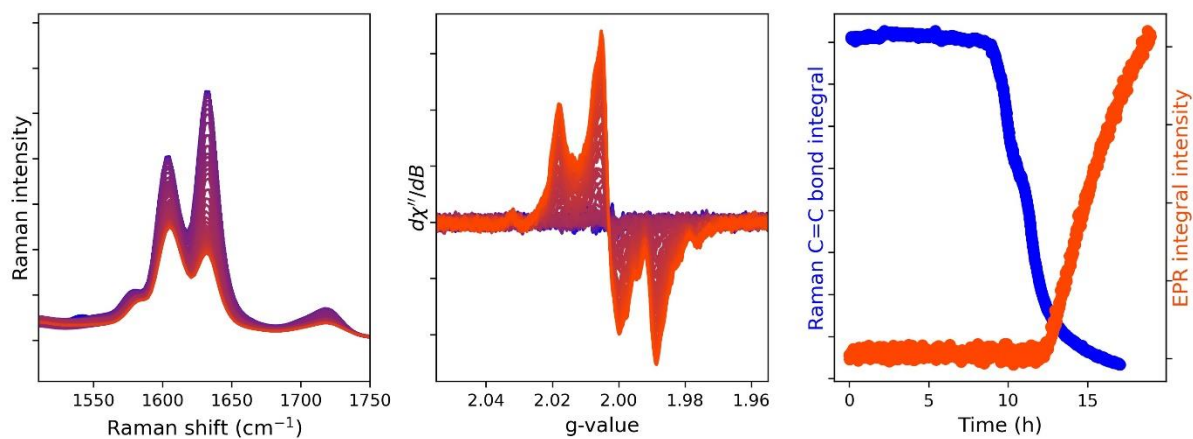


Figure S 5: Manganese-catalysed radical polymerization followed by Raman (left), EPR (centre) and the Raman (blue) and EPR (orange) integrals over time (right). Measurements were performed simultaneously on two different aliquots of the reaction. EPR parameters: power 0.01 mW (40 dB) gain 60 dB, sweep width 300 G, sweep time 90 s, 1 accumulation, 2 G modulation amplitude.

Simultaneous in-situ UV-Vis and Raman spectroscopy while curing

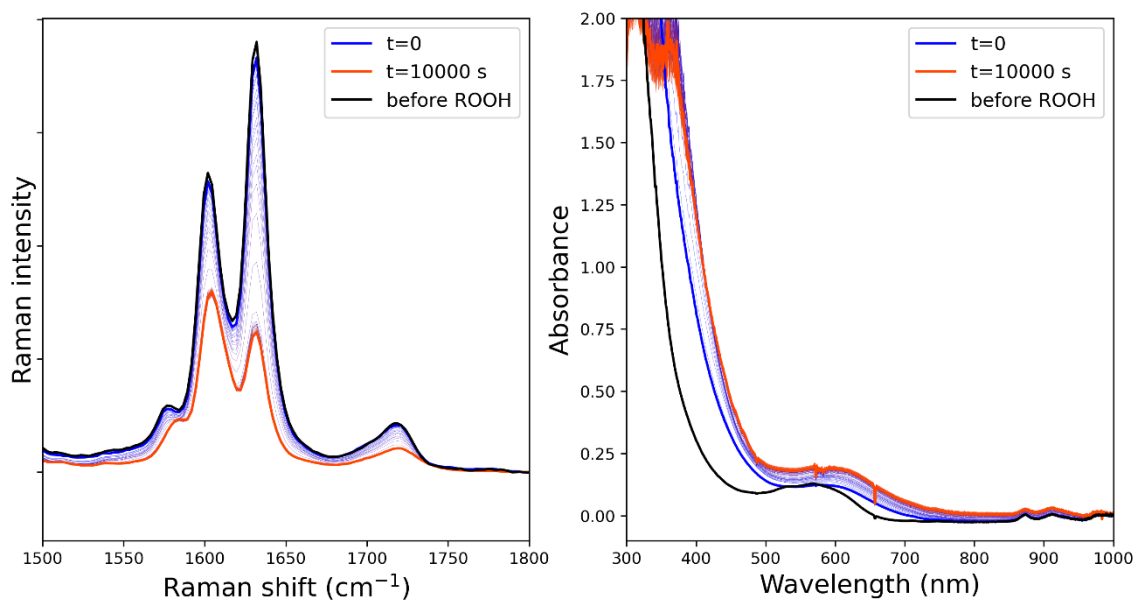


Figure S 6: Simultaneous in-situ Raman (left) and UV/Vis (right) spectroscopy. A baseline has been applied to both datasets at 1800 cm⁻¹ and 1000 nm respectively to account for an increased baseline due to scattering.

Power dependence of observed EPR signals

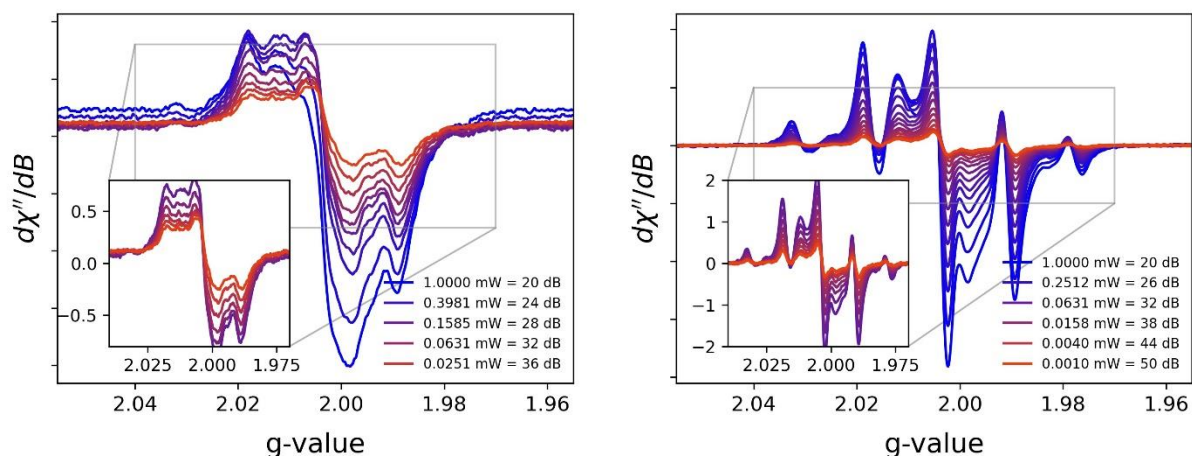


Figure S 7: Power dependence of a sample cured at room temperature (left) and after heating to 350K. Parameters (left): power 20-38 dB in steps of 2 dB, gain 40 dB, sweep width 400 G, sweep time 60 s, 5 accumulations, 1 G modulation amplitude. Parameters (right): power 20-50 dB in steps of 2 dB, gain 40 dB, sweep width 200 G, sweep time 30 s, 1 accumulation, 2 G modulation amplitude.

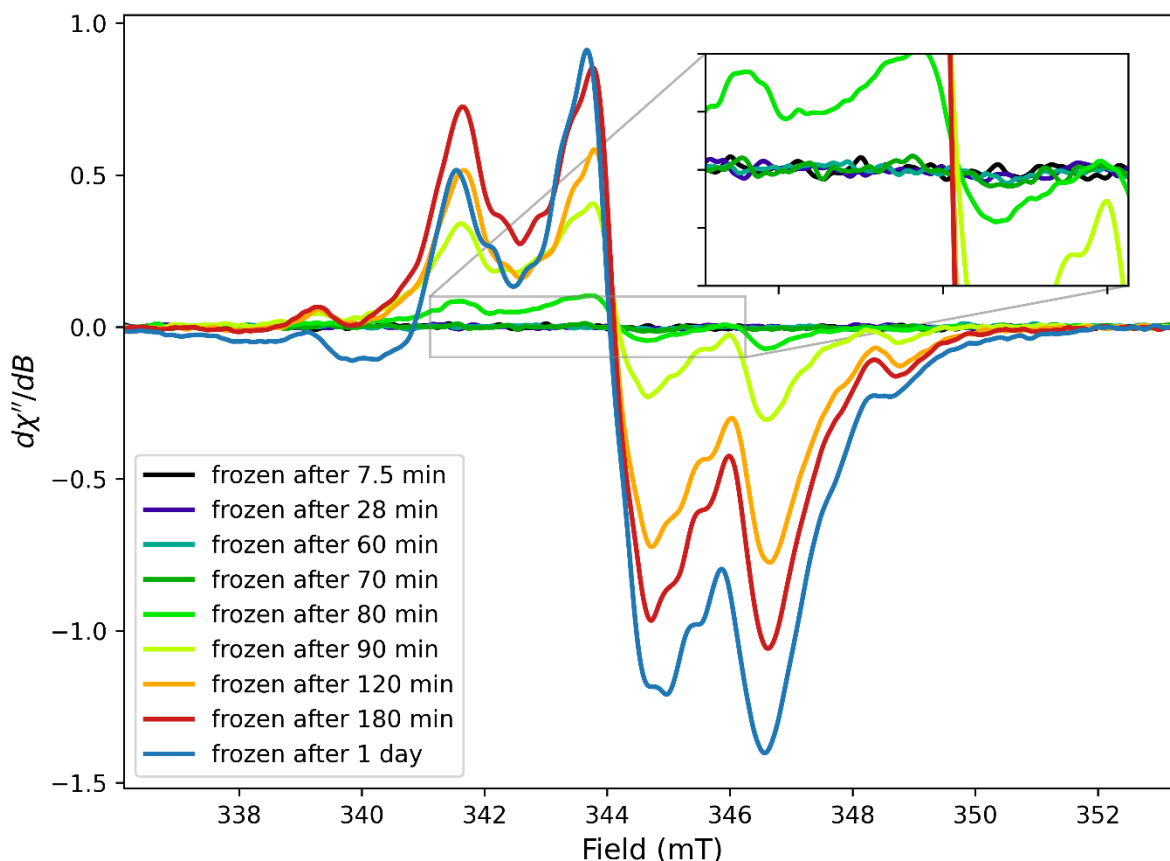


Figure S 8: EPR spectra (77 K) of samples flash-frozen at various times following addition of cumyl hydroperoxide to the reaction mixture. Parameters: power 0.0001 mW (60 dB), gain 60 dB, sweep width 300 G, sweep time 60 s, 5 accumulations, 2 G modulation amplitude. See figure 2 in main text for x-axis in g-value.

Observation of BHT in the resin

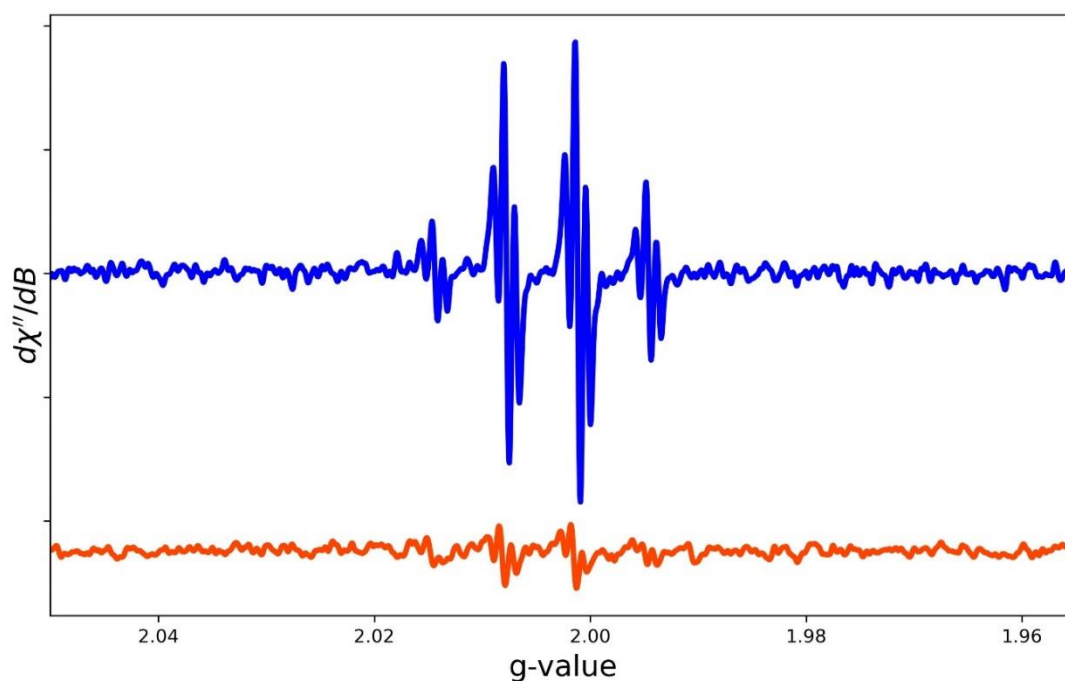


Figure S 9: BHT radical observed by EPR spectroscopy (blue: photoinitiated with Irgacure 819 and increased BHT concentration. Parameters: 0.3162 mW (25dB), gain 40 dB, sweepwidth 200 G, sweeptime 30 s, 10 accumulations, 1 G modulation amplitude, orange: under reaction conditions with D_8 -styrene. Parameters: 0.3162 mW (25 dB), gain 40 dB, sweepwidth 200 G, sweeptime 60 s, 5 accumulations, 1 G modulation amplitude).

Comparison between room-temperature cure and flash-frozen samples

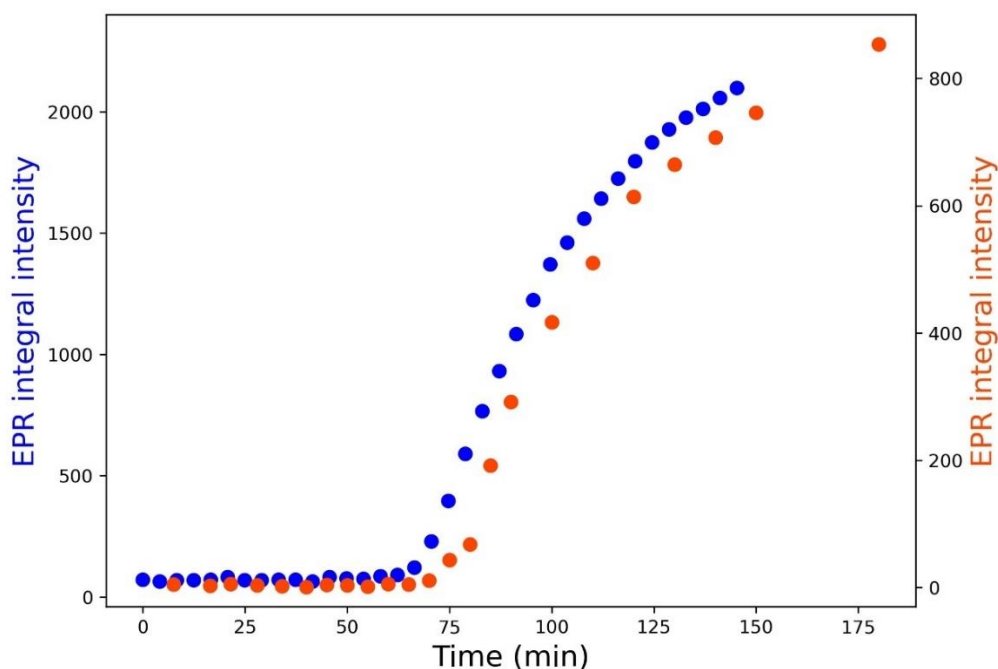


Figure S 10: Integration EPR signals of a sample held continuously in the EPR spectrometer recorded at 298 K (blue) and samples flash-frozen in $N_2(l)$ at specific time points recorded at 77 K (orange).

The slight off-set in time might be caused by the time taken to tune the sample in the EPR spectrometer.

Effect of Temperature on EPR signal intensity for $S = \frac{1}{2}$

The Boltzmann distribution gives the relative occupancy of two levels based on the temperature of the system and the relative energy between the two levels:

$$\frac{N_i}{N_j} = \frac{g_i}{g_j} \exp\left(\frac{-\Delta E_{ij}}{k_B T}\right)$$

Where N_i and N_j are the number of molecules in states i and j respectively, g_i and g_j are the degeneracies of both levels and $\Delta E_{ij} = E_i - E_j$. Applying this equation to EPR transition involving only $S = \frac{1}{2}$ systems there are only two states, which are nondegenerate when a magnetic field is applied. So:

$$\frac{N_+}{N_-} = \exp\left(\frac{-\Delta E}{k_B T}\right)$$

The EPR signal intensity is proportional to the excess number of spins, i.e., how many more spins there are in the spin up state compared to the spin down state, as each spin can do either absorption (when in the spin down state) or stimulated emission (when in the spin up state). This cancels most of the signal, but when we have a magnetic field there is some spin excess:

$$I_{\text{EPR}} \propto \Delta N = N_+ - N_-$$

If we consider that there is a constant total number of spins/radical N then $N_+ + N_- = N$. It can be shown by substituting equation 2 into that:

$$N_- = \frac{N}{1 + \exp\left(\frac{-\Delta E}{k_B T}\right)}$$

and

$$N_+ = \frac{N}{1 + \exp\left(\frac{\Delta E}{k_B T}\right)}$$

By substituting these equations:

$$\Delta N = N \left(\frac{1}{1 + \exp\left(\frac{\Delta E}{k_B T}\right)} - \frac{1}{1 + \exp\left(\frac{-\Delta E}{k_B T}\right)} \right)$$

and plotting this function versus temperature, the following curve is obtained:

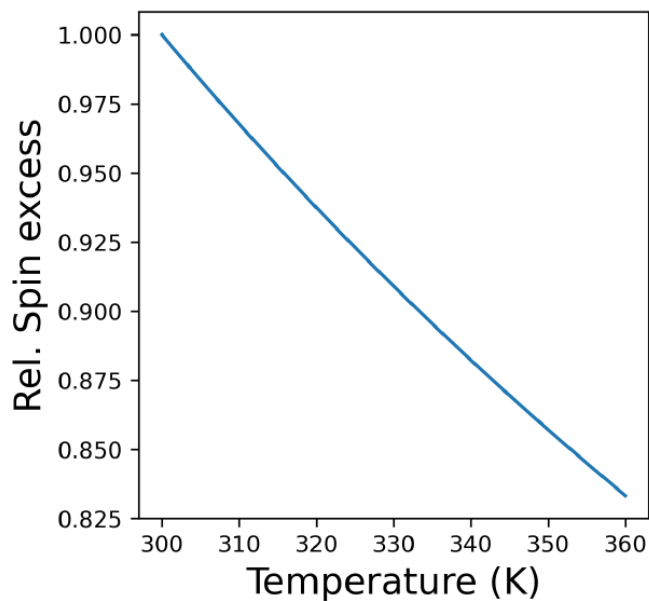


Figure S 11: Theoretical value of excess spins versus temperature (K).

An approximate 17% decrease of signal is expected when heating a sample from room temperature to 80 °C.

MCR analysis

MCR (multivariate curve resolution) was performed using the The UnscramblerX 10.5.1 software package (CAMO). The data was fitted well with 2 components, which resemble closely the styrene and BADGE-MA based radicals, and showed a time dependence of contribution revealing the contribution of the BADGE-MA radical increasing only after 40 min.

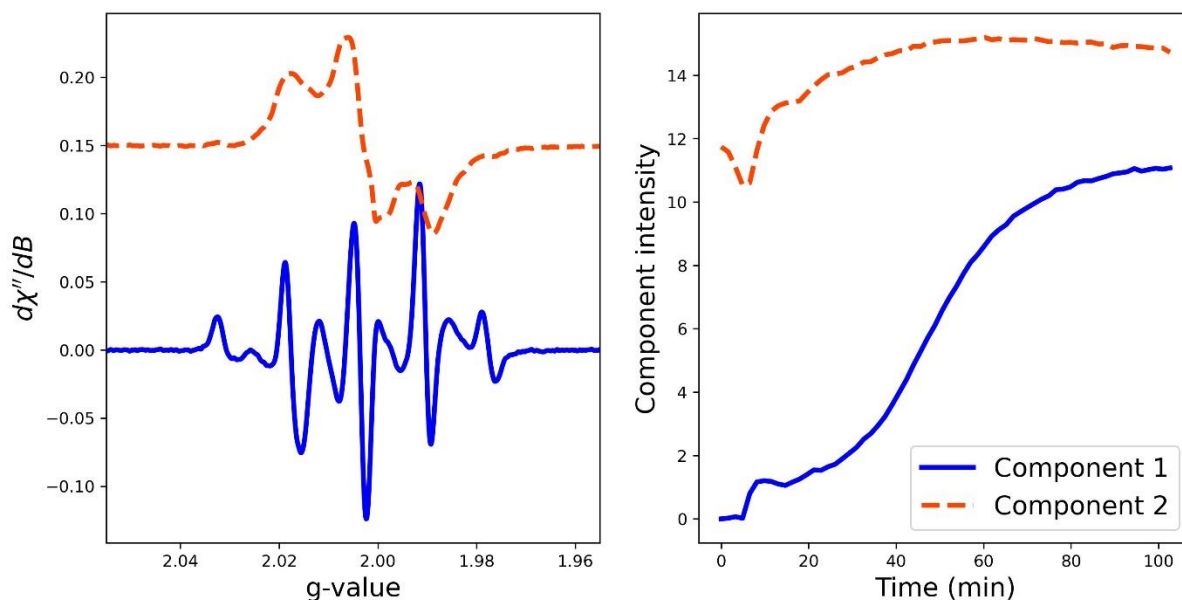


Figure S 12: Component spectra (left) and component concentrations (right) obtained by multivariate curve resolution.

Sample heated to 80 °C and subsequently cooled to room temperature

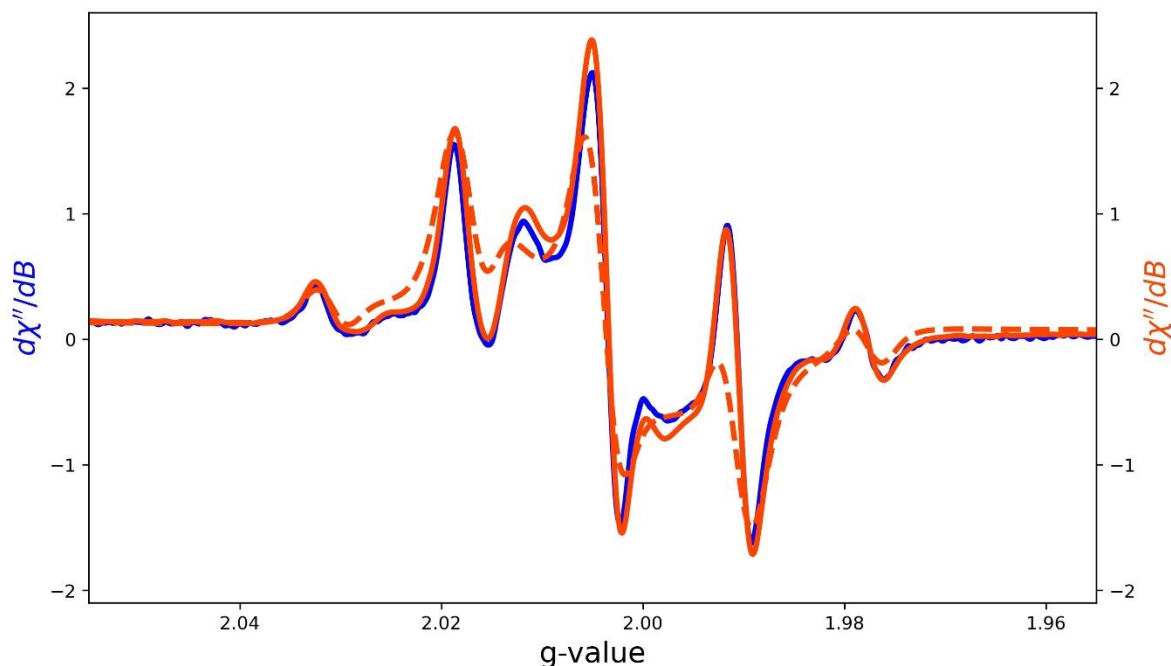


Figure S 13: EPR spectra of a sample kept at 350 K for 100 min at 350K (blue) and after subsequent cooling to room temperature (orange, solid), and fitted spectrum of sample cooled to room temperature (orange, dashed, Table S 4). Parameters at 350K: 0.01 mW (40 dB), gain 40 dB, sweep width 300 G, sweep time 90 s, 1 accumulation, 2 G modulation amplitude, parameters at room temperature: 0.01 mW (40 dB), gain 50 dB, sweep width 300 G, sweep time 90 s, 5 accumulations, 2 G modulation amplitude.

EPR fit parameters

Table S 1: fitting parameters of BADGE-MA/ethylbenzene (Figure 5, left)

	g	Nucs	A	lwpp	weight
MA1	2.0038, 2.0038, 2.0037	1H,1H,1H,1H	63.1458, 66.2191, 61.3802, 64.47	0.5559	0.045638
MA2	2.0039, 2.0039, 2.0037	1H,1H,1H,1H,1H	64.5332, 65.8619, 57.4097, 24.517, 23.0469	1.1	0.204614

Table S 2: Fitting parameters of BADGE-MA/styrene (Figure 5, center)

	g	Nucs	A	lwpp	weight
MA1	2.0038, 2.0038, 2.0037	1H,1H,1H,1H	63.1458, 66.2191, 61.3802, 64.47	0.5559	0.045638
MA2	2.0039, 2.0039, 2.0037	1H,1H,1H,1H,1H	64.5332, 65.8619, 57.4097, 24.517, 23.0469	1.1	0.204614
St	2.002106473459402, 2.005408258812338, 2.0018123603787106	1H,1H	47.46099184407326, 47.4586340290383	1.526228	2.244188

Table S 3: Fitting parameters of BADGE-MA/D₈-styrene (Figure 5, right)

	g	Nucs	A	lwpp	weight
MA1	2.0038, 2.0037 2.0038,	1H,1H,1H,1H	63.1458, 66.2191, 61.3802, 64.47	0.5559	0.045638
MA2	2.0039, 2.0037 2.0039,	1H,1H,1H,1H,1H	64.5332, 65.8619, 57.4097, 24.517, 23.0469	1.1	0.204614
St	2.005576094257932 2.0019272269757242 2.0018581861950473			0.839998	0.430744

Table S 4: Fitting parameters of a cured sample kept at 350K for 100 min (Figure 4 and Figure S 13)

	g	Nucs	A	lwpp	weight
MA1	2.0038, 2.0037 2.0038,	1H,1H,1H,1H	63.1458, 66.2191, 61.3802, 64.47	0.5559	0.045638
MA2	2.0039, 2.0037 2.0039,	1H,1H,1H,1H,1H	64.5332, 65.8619, 57.4097, 24.517, 23.0469	1.1	0.204614
St	2.002106473459402, 2.005408258812338, 2.0018123603787106	1H,1H	47.46099184407326, 47.4586340290383	1.526228	0.417353

Computational details

In a solid resin, the conformations that are observed can vary widely due to random packing, and hence a large number of atoms and molecules need to be included in the prediction. The approach taken. Structures were optimized and a conformer search was preformed using xtb's CREST method.² The 10 conformers with lowest energies (by XTB) were chosen that were not necessarily EPR equivalent due to symmetry.

The selected conformers were optimized using DFT, and EPR parameters were calculated, using Orca 4.2.1.³ with the B3LYP/EPR-II functional/basis set⁴, this same functional and basis set was used by Truffier-Boutry et al.⁵ For styrene based radicals, EPR calculation were performed with deuterated styrene, using the following parameters:

PPP=81.90634, QQQ=0.029, III=1.0

The spectra were generated using EasySpin⁶ from the calculated parameters with a cutoff coupling constant of 18 Hz for hydrogen spectra and 3 Hz for deuterated spectra. Spectra were calculated using the pepper function, which calculates solid powder EPR spectra by taking multiple orientations with the applied magnetic field with a peak-to-peak linewidth of 0.75 mT. From the energies and spectra a Boltzmann weighed spectra was created, by calculating the sum of occupancies of all conformers times the spectra. However, this may not be realistic as some conformers may not be present due to high barrier to their formation and hence not all conformers are calculated.

Raman band assignment of H₈-styrene, D₈-styrene and BADGE-MA

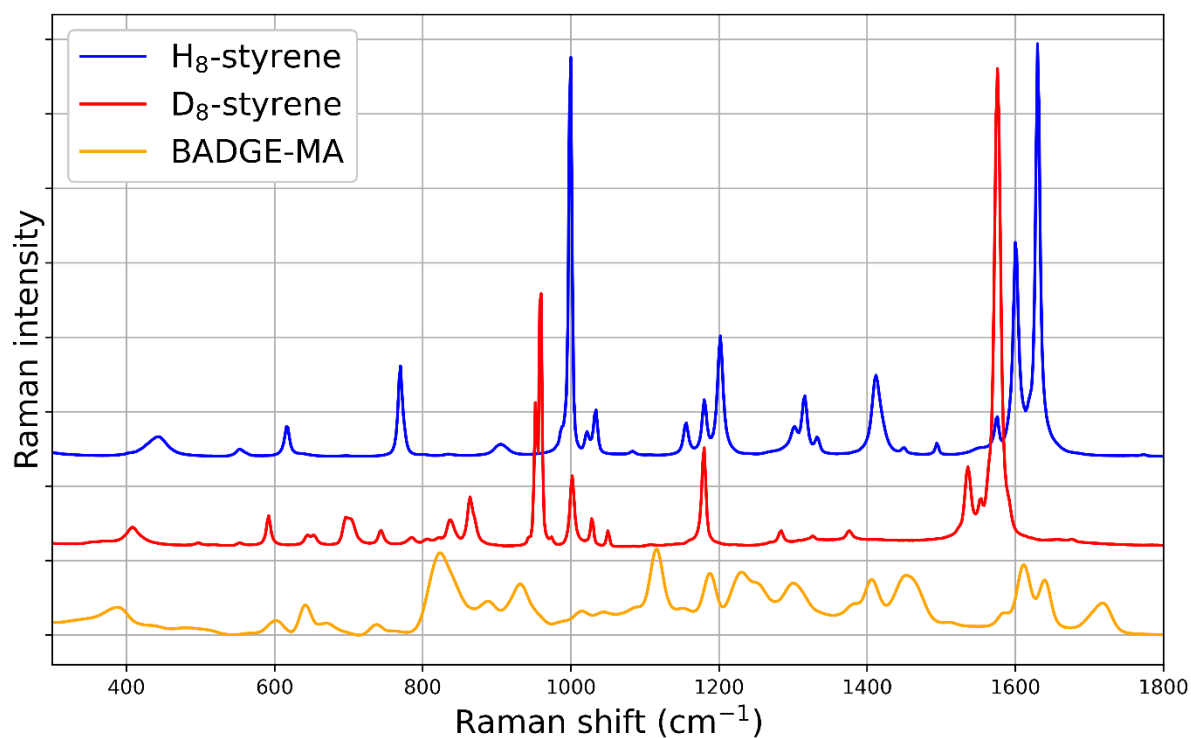


Figure S 14: Raman spectra of H₈-styrene, D₈-styrene and BADGE-MA.

Table S 5: Raman band assignment of H₈-styrene. Small deviations might be caused by variations in calibration.

Raman bands of H ₈ -styrene	Band assignment
617	Ring deformation
770	CH ₂ rocking
906	CH ₂ wagging
998	Ring C-C stretch
1033	Ring C-C stretch + CH ₂ rocking
1155	Ring C-H rocking
1180	Ring C-H rocking
1202	Aryl-vinyl C-C stretch
1315	Vinyl C-H rocking
1412	CH ₂ scissoring
1449	Ring C-C stretch/C-H bending. Contribution of CH ₂ scissoring
1496	Ring C-C stretch/C-H bending
1575	Ring C-C stretch
1601	Ring C-C stretch
1630	C=C stretch

Table S 6: Raman band assignment of D₈-styrene. Small deviations might be caused by variations in calibration.

Raman bands of D ₈ -styrene	Band assignment
592	Ring C-C bending
644	Ring mode
697	C-D bending (oop) and C-C stretch (in plane)
743	C-D bending (oop)
787	C-D bending (in plane or out of plane, not sure)
837	Ring C-D bending (in plane) and/or ring C-C out-of plane bending
864	Ring C-D bending (in plane)
959	Ring C-C stretch
1001	Vinyl C-D bending (in plane)
1029	C-D bending (in plane), CD ₂ scissoring
1051	C-D bending (in plane), CD ₂ scissoring
1180	C _{ring} -C _{vinyl} stretch
1284	Ring C-C stretch
1326	Ring C-C stretch
1376	Ring C-C stretch
1536	Ring C-C stretch
1553	Ring C-C stretch
1576	C=C stretch

Table S 7: Raman band assignment of BADGE-MA. Small deviations might be caused by variations in calibration.

Raman bands of BADGE-MA	Band assignment
601	Skeletal deformation
636	Ring deformation
733	Ring torsion
816	Ring CH ob
885	Core
932	Core
1013	Ring C-C stretch
1045	Ring C-C stretch, CH ₂ rocking
1112	Aryl-C-Aryl stretch
1188	COC distortion
1229	OCH ₂ C wagging
1251	Ring C-C stretch
1297	CH ₂ distortion
1378	CH ₃ distortion
1403	CH ₂ distortion
1460	CH ₂ distortion

1512	Ring C-C stretch
1582	Ring C-C stretch
1610	Ring C-C stretch
1638	C=C stretch
1717	C=O stretch

Iodometric determination of hydroperoxide concentration

Iodometric determination of oxidant concentration⁷⁻⁹ was done on a maximum of 12 samples using a Radley carousel 12 plus. Solutions of acetic acid (10%) in isopropanol (10 mL) and sodium iodide (NaI, saturated) in isopropanol (4 mL) were added to a reaction tube. To this, 500 μ L of sample was added. For viscous samples, the sample weight was used instead. Samples were refluxed for a minimum of 5 minutes. After cooling to room temperature, 2 mL of distilled water was added. Samples were diluted 20 times with isopropanol and a UV-Vis spectrum was recorded in a 2 mm path length quartz cuvette on a Specord210 (AnalytikJena). Within the concentration range of the experiment, the concentration of oxidant relates linearly to the absorption at 360 nm. The styrene/BADGE-MA or styrene/methyl methacrylate reaction mixture before addition of cumene hydroperoxide was used as a blank. Calibration was performed in the range of 0-120 μ mol/g cumene hydroperoxide (initial concentration in styrene/BADGE-MA/Co(II) 2-ethylhexanoate and styrene/methyl methacrylate/Co(II) 2-ethylhexanoate mixtures was 92 μ mol/g).

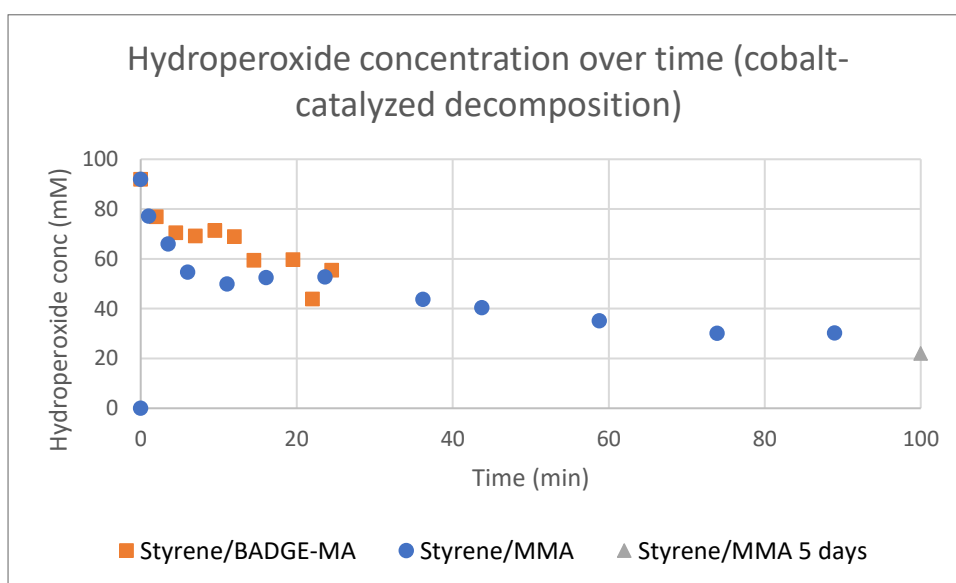


Figure S 15: Hydroperoxide concentration over time as determined iodometrically for cobalt catalyzed cumene hydroperoxide determination in styrene/BADGE-MA (orange), styrene/methyl methacrylate (blue). The concentration of residual oxidant after 5 days was also determined (grey).

Effect of temperature on curing progress

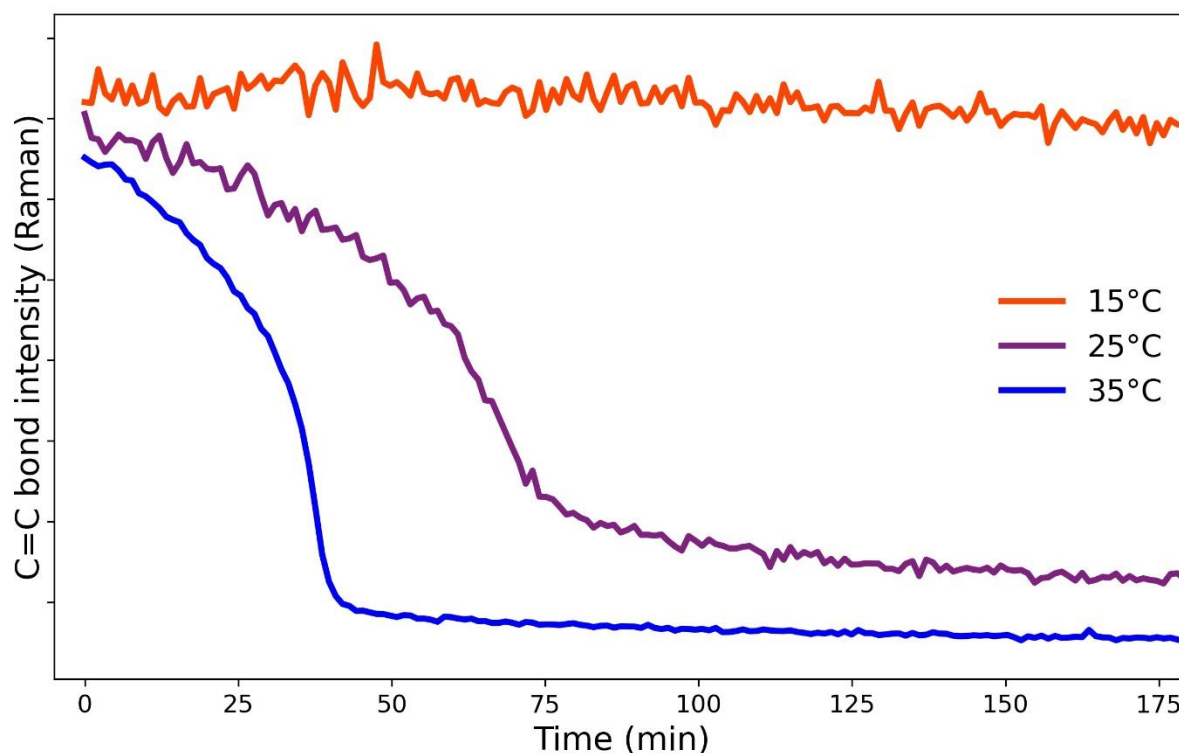


Figure S 16: C=C bond disappearance as observed by Raman spectroscopy at several temperatures (orange: 15°C, purple: 25°C, blue: 35°C).

Combined Raman and EPR spectroscopy of BADGE-MA/ethylbenzene curing

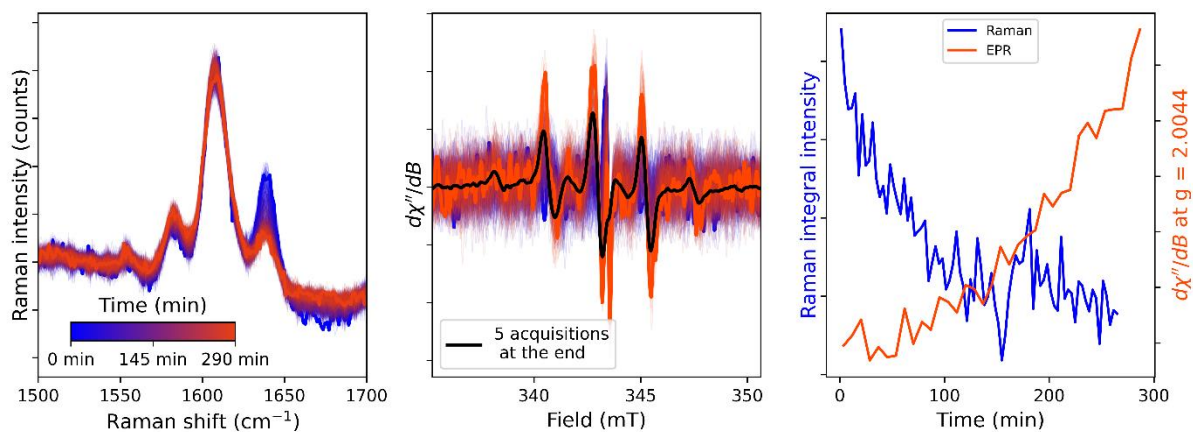


Figure S 17: Simultaneous in situ Raman (left) and EPR (middle) spectroscopy during polymerization at room temperature. The C=C stretch integral and EPR integral over time (right) show the emergence of the EPR signal as the C=C stretch conversion comes to a halt. EPR parameters: 0.01 mW (40 dB), gain 50 dB, sweep width 300 G, sweep time 90 s, 1 accumulation, 2 G modulation amplitude.

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