

Supplementary Information

Table S1. Main aqueous reactions and rate constants in MVK + HO[•] initial reaction systems

Reactions	Label	Rate constant 25°C
$\text{H}_2\text{O}_2 + \text{h}\nu \xrightarrow{\text{J}} 2 \text{HO}^\bullet$	R1	$\text{J}^{\text{a}} = 8.5 \times 10^{-6} \text{ s}^{-1}$
$\text{H}_2\text{O}_2 + \text{HO}^\bullet \xrightarrow{k_2} \text{HO}_2^\bullet + \text{H}_2\text{O}$	R2	$k_2 = 2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$
$\text{HO}_2^\bullet + \text{HO}_2^\bullet \xrightarrow{k_3} \text{H}_2\text{O}_2 + \text{O}_2$	R3	$k_3 = 8.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$
$\text{HO}_2^\bullet + \text{O}_2^\bullet + \text{H}^+ \xrightarrow{k_4} \text{H}_2\text{O}_2 + \text{O}_2$	R4	$k_4 = 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$
$\text{MVK} + \text{HO}^\bullet \xrightarrow{k_{\text{mvk}}} \text{Products}$	R5	$k_{\text{MVK}} = 7.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$

a: Hydrogen peroxide photolysis rate (J) was determined by fitting H₂O₂ loss in H₂O₂+UV control experiments

Table S2. Synthesis of oligomers of MVK. Using a water soluble synthetic radical initiator (V50), we synthesized an oligomer of MVK. Experimental conditions of MVK-oligomerization using a water soluble synthetic.

[MVK] ₀	[V50] ₀	[O ₂] ₀	Temp. 1 (°C)	Temp. 2 (°C)
240 mM	3 mM			
24 mM	0.3 mM	Low O ₂ ^a	50°C from 0 to 30 min of reaction	70°C from 30 to 120 min of reaction
0.24 mM	0.03 mM			

^a 30 min prior to the start of the reaction, the solutions were degassed using an argon flow, in order to prevent from O₂ inhibiting the oligomer formation (Decker and Jenkins, 1985). 2,2'-Azobis(2-methylpropionamidine) forms two symmetric initiator radicals by thermal homolysis on N=N (Reaction 6). MVK polymerization on the Azo initiator radical (Reaction 7).

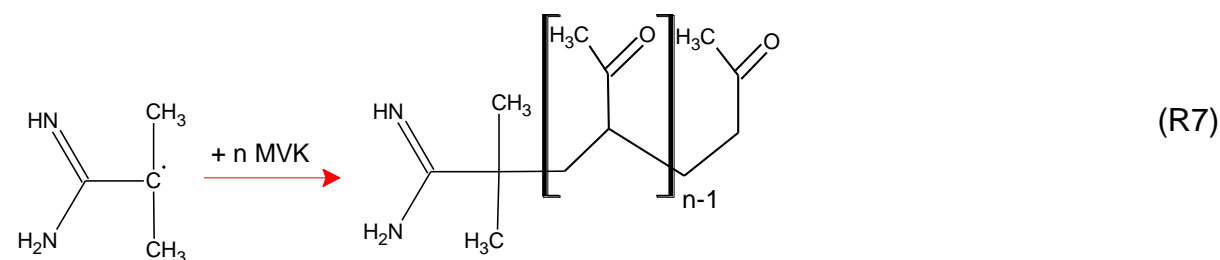
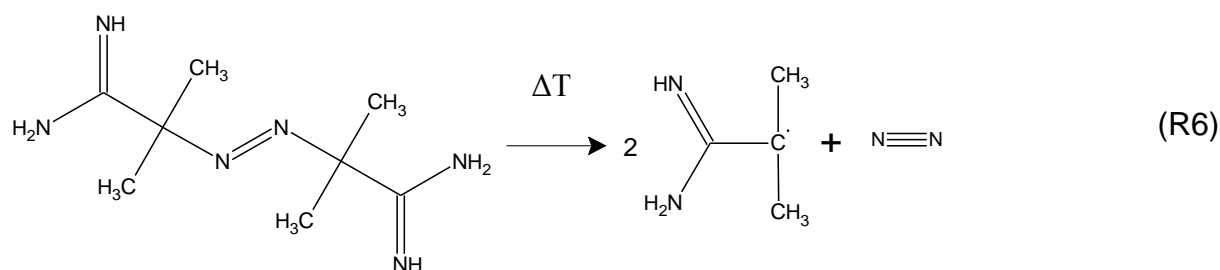


Fig. S1. UV-visible absorption spectra (from 190 to 400 nm) of aqueous solutions of MVK (24 mM) + V-50 (0.3 mM), before (at $t=0$) and after (at $t = 120$ min) MVK radical oligomerization synthesis using the conditions indicated in Table S2. Solutions were diluted 100 times for the spectra at 211 nm (violet and red spectra).

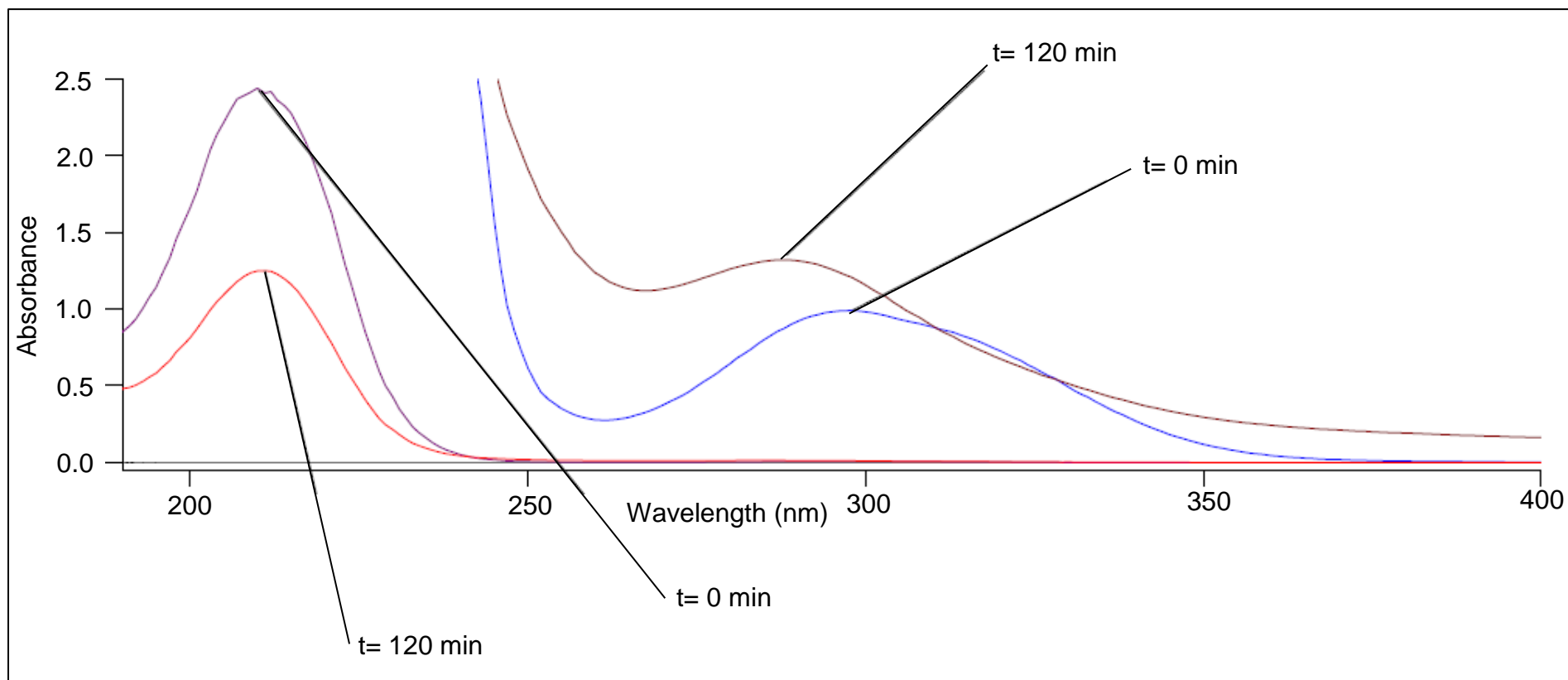


Fig. S2. Mass spectrum (obtained using UPLC-ESI-MS) for the retention time range 0-5 min, in the positive mode, after MVK radical oligomerization synthesis using the conditions indicated in Table S2 (24mM). The series highlighted in blue is obtained from MVK polymerization on the Azo initiator radical (Reaction 2).

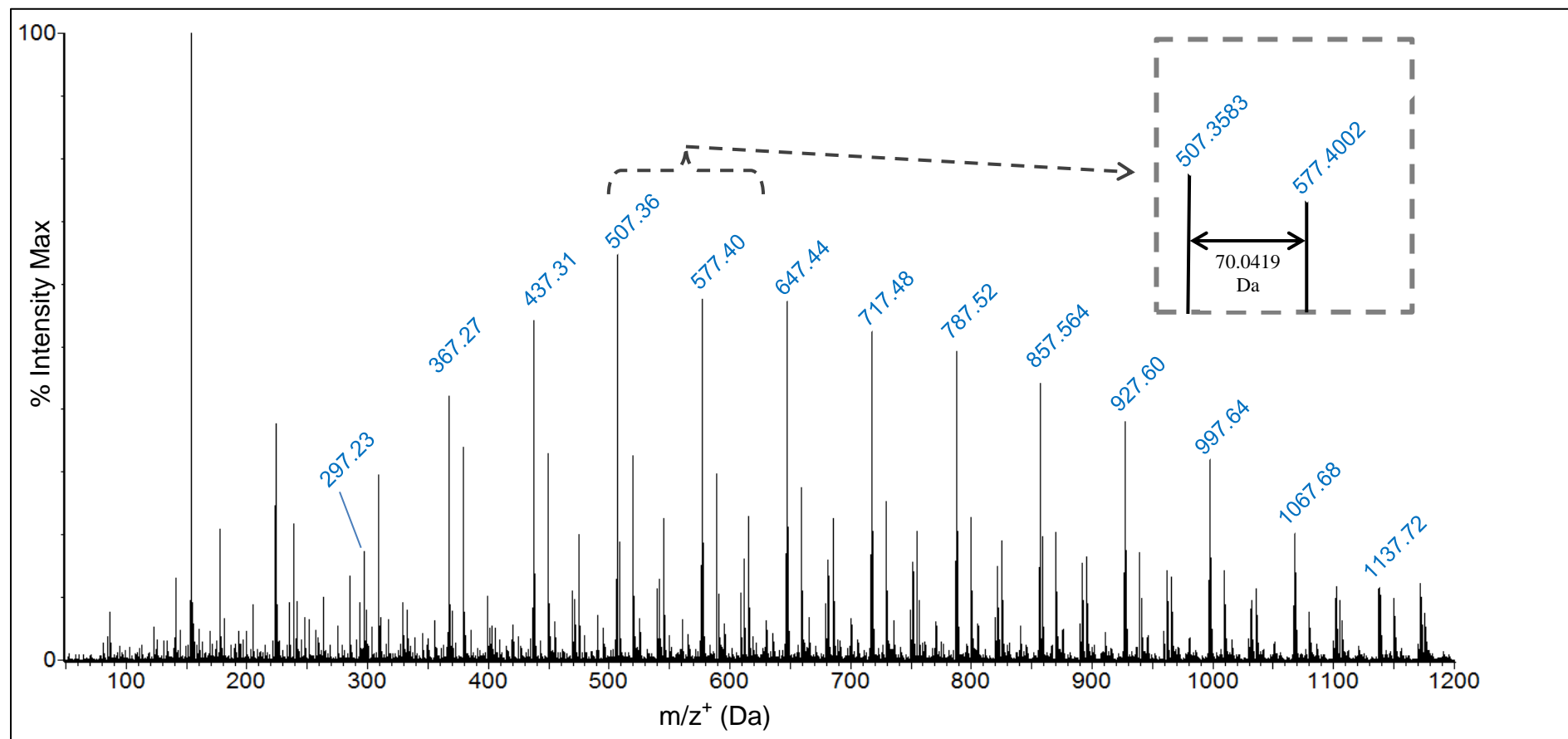


Fig. S3. Extracted ESI chromatogram (using UPLC-ESI-MS) of one series (S174) of oligomers formed during OH-oxidation of MVK (experiment A) after 50 min of reaction. This series corresponds to the red one in Figure 1. Only one peak out of two (i.e. odd n) is shown here for clarity, up to $n = 15$.

