Electronic Supplementary Material (ESI) for Polymer Chemistry.

Role of ketyl radicals in free radical photopolymerization: new experimental and theoretical insights

Electronic Supporting Information

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Quenching of ^{3}ITX by NPG

Two quenching experiments were averaged and the $k_q^{3ITX/NPG}$ finally obtained by the Stern-Volmer analysis is equal to **6.0×10^9 M^{-1}.s^{-1}**.

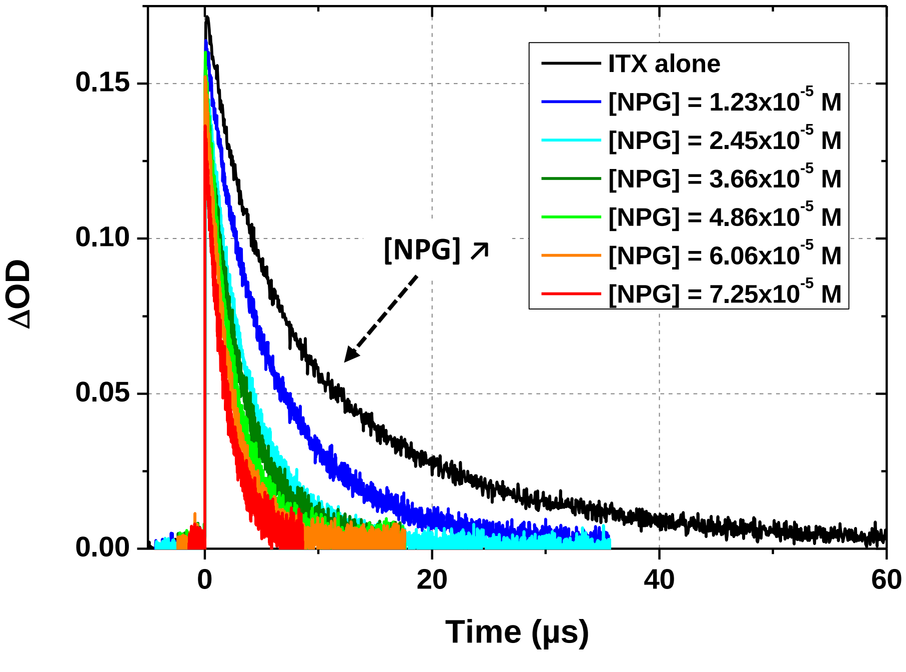


Figure S1: Evolution of the ITX triplet state transient signal at 640 nm with increasing NPG concentrations (λ_{ex} = 355 nm, 5-6 mJ/pulse, OD^i_{355nm}(ITX) = 0.11, Ar).

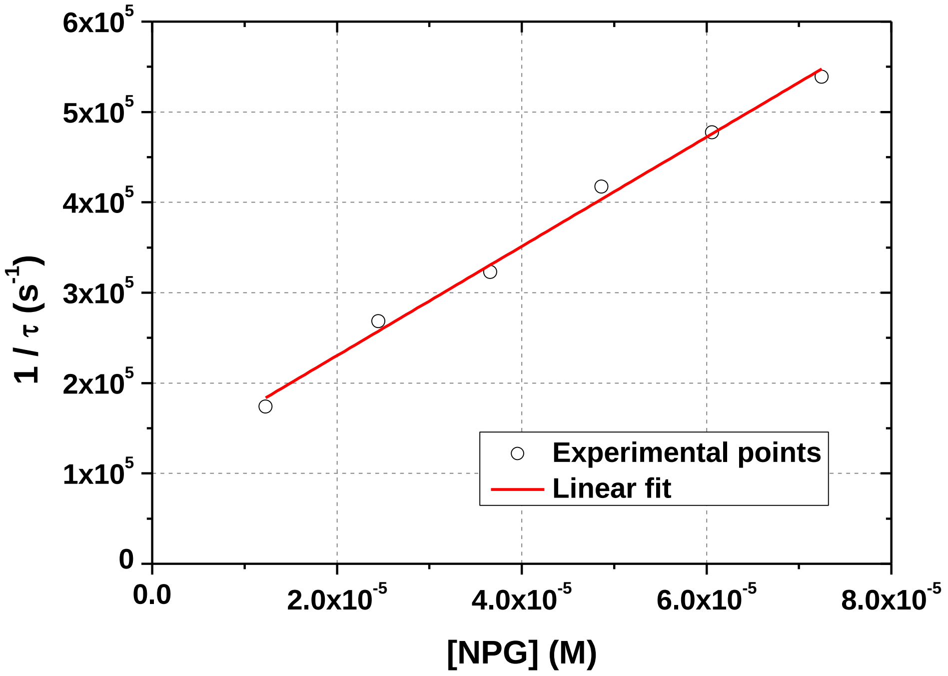


Figure S2: Stern-Volmer plot of the evolution of ITX triplet lifetime τ with increasing NPG concentrations.

Reaction ITXH$^\bullet$ + O_2

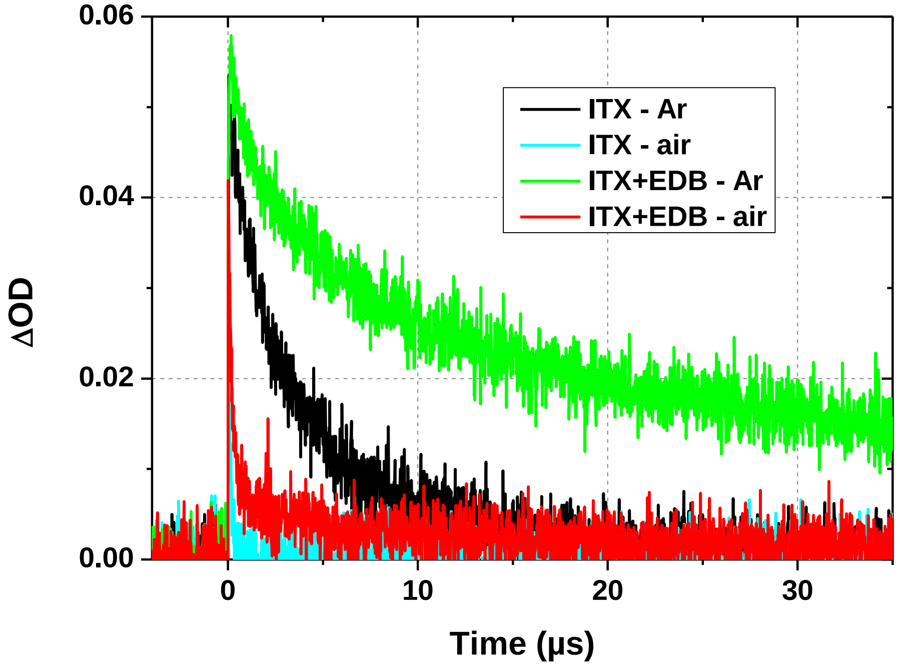


Figure S3: Transient absorption kinetics recorded at 470 nm for solutions of ITX under Ar (–) and air (–), and ITX+EDB under Ar (–) and air (–) in acetonitrile (λ_{ex} = 355 nm, 6-7 mJ/pulse).

Development of the kinetic model

The propagation (k_p), bimolecular termination ($k_{t,b}$), initiation (k_i) and primary radical termination ($k_{t,PRT}$) kinetic rate constants are defined as functions of the fractional free volume ν_f in order to take into account their progressive diffusional control throughout the photopolymerization process.[S1-4] ν_f represents the fraction of unoccupied volume in the reaction medium, and decreases as the monomer is converted into a polymer according to:

$$\nu_f = 0.025 + \alpha_M (T - T_{g,M}) \Phi_M + \alpha_P (T - T_{g,P})(1 - \Phi_M) \tag{S1}$$

$$\Phi_M = \frac{1 - \mathrm{Conv}}{1 - \mathrm{Conv} + \mathrm{Conv} \times \left({}^{\rho_M}/_{\rho_P} \right)} \tag{S2}$$

Subscripts M and P refer to monomer and polymer respectively, with α the thermal expansion coefficient (difference between liquid and glassy state expansion coefficients), T_g the glass transition temperature, Φ the volume fraction and ρ the volumetric mass density.

The expressions for the propagation (k_p) and bimolecular termination ($k_{t,b}$) rate constants are given in Eqs. S3 and S4.[S1-4] The expression of $k_{t,b}$ includes both diffusional bimolecular termination and subsequent reaction diffusion processes. k_{p0} and $k_{t,b0}$ correspond to the propagation and bimolecular termination intrinsic rate constants respectively, i.e. without any diffusional control. A_p and $A_{t,b}$ are the parameters which govern the rate at which, respectively, k_p and $k_{t,b}$ decrease with viscosity. Finally, $\nu_{f,cp}$ and $\nu_{f,ct,b}$ represent the critical fractional free volumes at which propagation and bimolecular termination become diffusion-limited respectively.

$$k_p = \frac{k_{p0}}{\left(1 + \exp\left(A_p \left(\frac{1}{\nu_f} - \frac{1}{\nu_{f,cp}} \right) \right) \right)} \tag{S3}$$

$$k_{t,b} = k_{t,b0} \left(1 + \frac{1}{\frac{R_{rd} k_p [C{=}C]}{k_{t,b0}} + \exp\left(-A_{t,b} \left(\frac{1}{\nu_f} - \frac{1}{\nu_{f,ct,b}} \right) \right)} \right)^{-1} \tag{S4}$$

The initiation rate constant k_i (Eq. S5) and the PRT rate constant $k_{t,PRT}$ (Eq. S6) have the same expression as the propagation rate k_p with appropriate subscripts. The exponential factors A and the critical fractional free volume $\nu_{f,c}$ coefficients for initiation and PRT are taken equal to A_p and $\nu_{f,cp}$.[S5] The values of the initiation (k_{i0}) and PRT ($k_{t,PRT0}$) intrinsic rate constants depend on the nature of the primary initiating radical.

$$k_i = \frac{k_{i0}}{\left(1 + \exp\left(A_i \left(\frac{1}{\nu_f} - \frac{1}{\nu_{f,ci}} \right) \right) \right)} \tag{S5}$$

$$k_{t,PRT} = \frac{k_{t,PRT0}}{\left(1 + \exp\left(A_{t,PRT}\left(\frac{1}{\nu_f} - \frac{1}{\nu_{f,ct,PRT}}\right)\right)\right)} \tag{S6}$$

The set of differential equations associated to the basic kinetic model defined in Figure 4 of the main paper is defined as:

$$\begin{aligned}\frac{d[{}^{0}ITX]}{dt} = &-\frac{{I_0}^{s}}{z}\left(1 - 10^{-\varepsilon(ITX)z[{}^{0}ITX]}\right) - k_{sq}[{}^{0}ITX][{}^{3}ITX] + {}^{1}k_{dea}[{}^{1}ITX] + {}^{3}k_{dea}[{}^{3}ITX] \\ &+ {k_{O_2}}^{{}^{3}ITX}[{}^{3}ITX][O_2] + k_{TTA}[{}^{3}ITX]^2 + k_{disp}[ITXH^{\bullet}]^2 + {k_{O_2}}^{ITXH^{\bullet}}[ITXH^{\bullet}][O_2]\end{aligned}$$

$$\frac{d[{}^{1}ITX]}{dt} = \frac{{I_0}^{s}}{z}\left(1 - 10^{-\varepsilon(ITX)z[{}^{0}ITX]}\right) - {}^{1}k_{dea}[{}^{1}ITX] - k_{ISC}[{}^{1}ITX] + k_{TTA}[{}^{3}ITX]^2$$

$$\begin{aligned}\frac{d[{}^{3}ITX]}{dt} = &\,k_{ISC}[{}^{1}ITX] - {}^{3}k_{dea}[{}^{3}ITX] - {k_{O_2}}^{{}^{3}ITX}[{}^{3}ITX][O_2] - 2k_{TTA}[{}^{3}ITX]^2 - k_{sq}[{}^{0}ITX][{}^{3}ITX] \\ &- k_{diff}[{}^{3}ITX][AH] + k_{-diff}[{}^{3}(ITX\text{- -}AH)]\end{aligned}$$

$$\frac{d[AH]}{dt} = -\,k_{diff}[{}^{3}ITX][AH] + k_{-diff}[{}^{3}(ITX\text{- -}AH)]$$

$$\frac{d[{}^{3}(ITX\text{- -}AH)]}{dt} = k_{diff}[{}^{3}ITX][AH] - k_{-diff}[{}^{3}(ITX\text{- -}AH)] - {k_{-H}}^{{}^{3}ITX/AH}[{}^{3}(ITX\text{- -}AH)]$$

$$\begin{aligned}\frac{d[A^{\bullet}]}{dt} = &\,{k_{-H}}^{{}^{3}ITX/AH}[{}^{3}(ITX\text{- -}AH)] - {k_{O_2}}^{A^{\bullet}}[A^{\bullet}][O_2] - {k_i}^{A^{\bullet}}[A^{\bullet}][C{=}C] - {k_{t,PRT}}^{A^{\bullet}}[A^{\bullet}][R(C{=}C)_n{}^{\bullet}] \\ &- 2{k_{comb}}^{A^{\bullet}}[A^{\bullet}]^2 - {k_{comb}}^{A^{\bullet}/ITXH^{\bullet}}[A^{\bullet}][ITXH^{\bullet}]\end{aligned}$$

$$\begin{aligned}\frac{d[ITXH^{\bullet}]}{dt} = &\,{k_{-H}}^{{}^{3}ITX/AH}[{}^{3}(ITX\text{- -}AH)] - {k_{O_2}}^{ITXH^{\bullet}}[A^{\bullet}][O_2] - {k_i}^{ITXH^{\bullet}}[A^{\bullet}][C{=}C] \\ &- 2{k_{comb}}^{ITXH^{\bullet}}[ITXH^{\bullet}]^2 - {k_{comb}}^{A^{\bullet}/ITXH^{\bullet}}[A^{\bullet}][ITXH^{\bullet}]\end{aligned}$$

$$\begin{aligned}\frac{d[R(C{=}C)_n{}^{\bullet}]}{dt} = &\,{k_i}^{A^{\bullet}}[A^{\bullet}][C{=}C] + {k_i}^{ITXH^{\bullet}}[ITXH^{\bullet}][C{=}C] - 2k_{t,b}[R(C{=}C)_n{}^{\bullet}]^2 \\ &- {k_{t,PRT}}^{A^{\bullet}}[A^{\bullet}][R(C{=}C)_n{}^{\bullet}] - {k_{O_2}}^{R(C=C)_n{}^{\bullet}}[R(C{=}C)_n{}^{\bullet}][O_2]\end{aligned}$$

$$\frac{d[C{=}C]}{dt} = -{k_i}^{A^{\bullet}}[A^{\bullet}][C{=}C] - {k_i}^{ITXH^{\bullet}}[ITXH^{\bullet}][C{=}C] - k_p[C{=}C][R(C{=}C)_n{}^{\bullet}]$$

$$\begin{aligned}\frac{d[O_2]}{dt} = &-{k_{O_2}}^{{}^{3}ITX}[{}^{3}ITX][O_2] - {k_{O_2}}^{A^{\bullet}}[A^{\bullet}][O_2] - {k_{O_2}}^{ITXH^{\bullet}}[ITXH^{\bullet}][O_2] \\ &- {k_{O_2}}^{R(C=C)_n{}^{\bullet}}[R(C{=}C)_n{}^{\bullet}][O_2]\end{aligned}$$

Finally, the kinetic parameters used for the simulations are listed in Table S1.

Table S1: Parameters used for the simulations.

Parameter	Value	Unit	Source
T	20	°C	Experimental conditions
η_0	200	mPa.s	[S6]
B_η	2	/	[S7]
z	25	µm	Experimental conditions
I_0^s	10	$mW.cm^{-2}$	Experimental conditions
λ_{irr}	395	nm	Experimental conditions
$\varepsilon^{395\ nm}(ITX)$	2 900	$M^{-1}.cm^{-1}$	[S7]
Φ_{ISC}	0.85	/	[S8]
τ_S	150	ps	[S7]
τ_T	1.7	µs	[S7]
$^1k_{dea}$	1.0×10^9	s^{-1}	Equations from [S9]
$^3k_{dea}$	5.9×10^5	s^{-1}	Equations from [S9]
k_{ISC}	5.7×10^9	s^{-1}	Equation from [S9]
k_{sq}	5×10^8	$M^{-1}.s^{-1}$	[S7]
k_{TTA}	$(7 \pm 3)\times10^9$	$M^{-1}.s^{-1}$	[S8]
$k_{-H}^{3ITX/EDB}$	2.8×10^9	s^{-1}	Extracted from $k_q^{3ITX/EDB}$ [S10]
$k_{-H}^{3ITX/NPG}$	7.0×10^9	s^{-1}	Extracted from $k_q^{3ITX/NPG}$
$T_{g,M}$	-37	°C	[S7]
$T_{g,P}$	67	°C	Supplier information
ρ_M	1.1414	$g.cm^{-3}$	Supplier information
ρ_P	1.25	$g.cm^{-3}$	[S7]
α_M	0.0005	$°C^{-1}$	[S11,12]
α_P	0.000075	$°C^{-1}$	[S11,12]
M_{SR349}	455	$g.mol^{-1}$	Supplier information
k_{p0}	2.0×10^4	$M^{-1}.s^{-1}$	[S7]
A_p	1.05	/	[S7]
$\nu_{fc,p}$	0.0405	/	[S7]
$k_{i0}^{EDB\text{-}H\bullet}$	5.0×10^5	$M^{-1}.s^{-1}$	[S13]

$k_{i0}^{NPG\text{-}H\bullet}$	6.5×10^{5}	$M^{-1}.s^{-1}$	[S13]
$k_{i0}^{ITXH\bullet}$	40	$M^{-1}.s^{-1}$	[S8]
A_i	A_p	/	Assumptions in [S5]
$\nu_{fc,i}$	$\nu_{fc,p}$	/	Assumptions in [S5]
$k_{t,PRT0}^{A\bullet}$	k_{diff0}	$M^{-1}.s^{-1}$	/
$A_{t,PRT}$	A_p	/	Assumptions in [S5]
$\nu_{fc,t,PRT}$	$\nu_{f,cp}$	/	Assumptions in [S5]
$k_{t,b0}$	k_{diff0}	$M^{-1}.s^{-1}$	/
$A_{t,b}$	2.1	/	Proportionality with A_p [S2]
$\nu_{fc,t,b}$	0.059	/	Proportionality with $\nu_{fc,p}$ [S2]
R_{rd}	4	M^{-1}	[S7]
$[ITX]_0$	4.5×10^{-3} (0.1 wt%)	M	Experimental conditions
$[EDB]_0$ or $[NPG]_0$	1.5×10^{-2}	M	Experimental conditions
$[C{=}C]_0$	4.52	M	Experimental conditions
$[O_2]_0$	3.2×10^{-4}	M	[S7]

As previously assumed, the rate constant for all the oxygen inhibition reactions, as well as the radical-radical reactions ($A^\bullet + A^\bullet$, $ITXH^\bullet + ITXH^\bullet$ or $A^\bullet + ITXH^\bullet$ combination) are taken equal to the diffusion rate constant k_{diff} given by the Stokes-Einstein equation (Eq. 11 of the main paper).[S7] The viscosity is proposed to decrease exponentially with the conversion,[S14] with an exponential factor B_η previously optimized to 2 with other type-II photoinitiating systems.[S7]

Comparison with experiment – basic kinetic model (ITX+NPG)

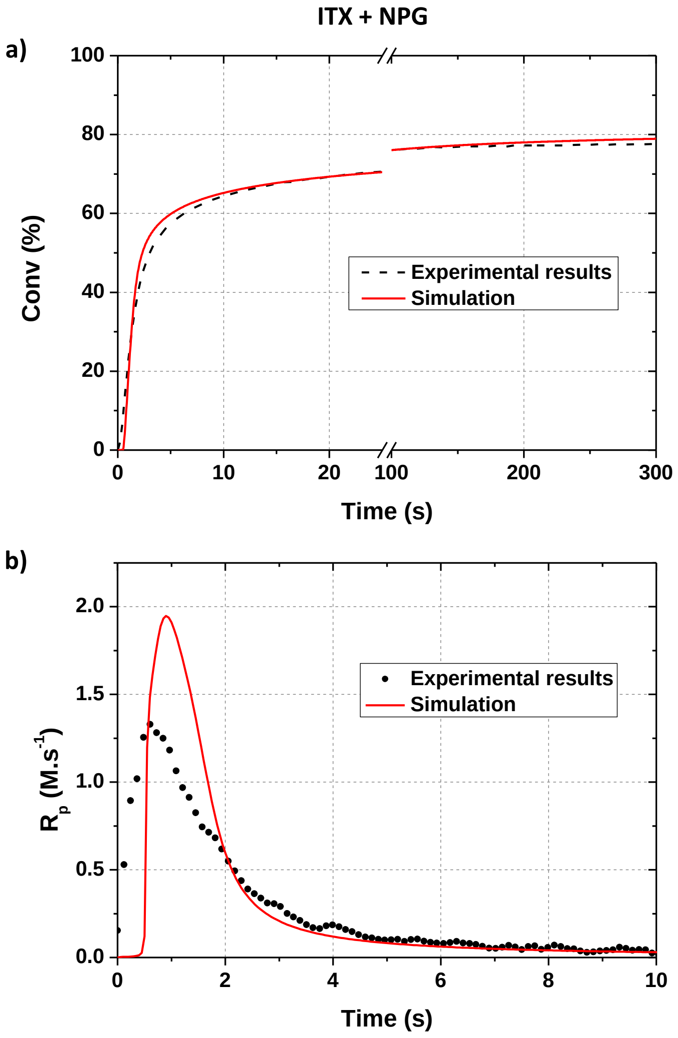


Figure S4: Comparison between experimental (dashed black) and simulated (plain red) a) acrylate double bond conversion b) rate of polymerization for ITX+NPG photoinitiating system – basic kinetic model (λ_{irr} = 395 nm, 10 mW.cm^{-2}, 0.1 wt% ITX / 1.5×10^{-2} M NPG).

Oxygen consumption in the presence of amines – effect of the AOO$^\bullet$ + AH reaction (ITX+EDB and ITX+NPG)

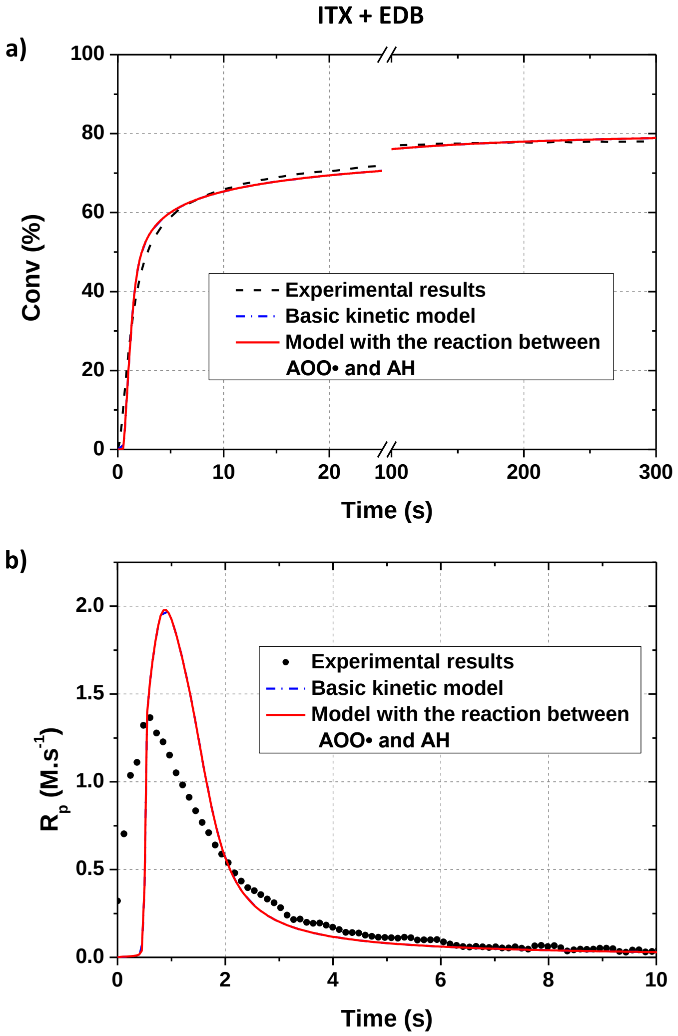


Figure S5: Comparison between experimental (dashed black) and simulated a) acrylate double bond conversion b) rate of polymerization for ITX+EDB photoinitiating system – basic kinetic model (dashed-dotted blue) and model with AOO$^\bullet$ + AH reaction (plain red) (λ_{irr} = 395 nm, 10 mW.cm^{-2}, 0.1 wt% ITX / 1.5×10^{-2} M EDB).

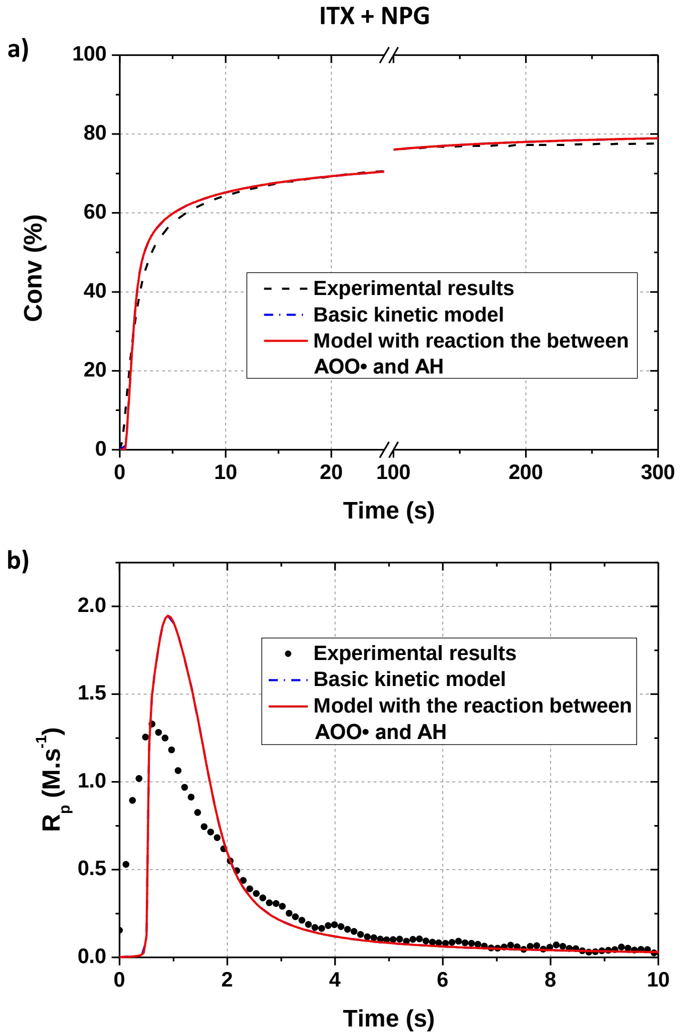


Figure S6: Comparison between experimental (dashed black) and simulated a) acrylate double bond conversion b) rate of polymerization for ITX+NPG photoinitiating system – basic kinetic model (dashed-dotted blue) and model with AOO$^{\bullet}$ + AH reaction (plain red) (λ_{irr} = 395 nm, 10 mW.cm^{-2}, 0.1 wt% ITX / 1.5×10^{-2} M NPG).

Oxygen consumption in the presence of amines – effect of the $R(C=C)_nOO^{\bullet}$ + AH reaction (ITX+NPG)

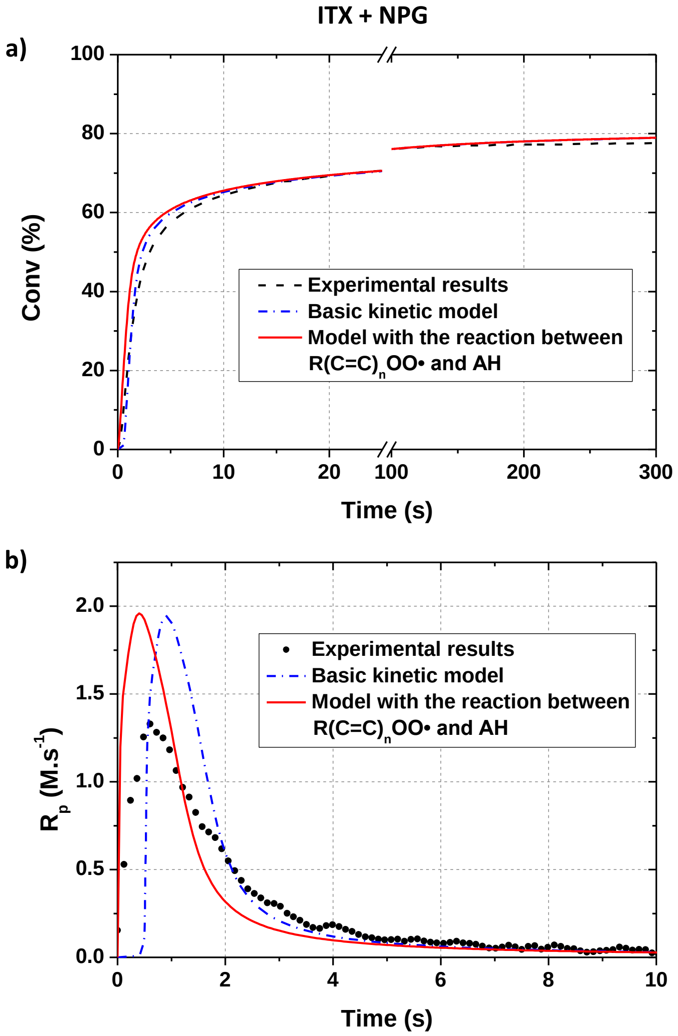


Figure S7: Comparison between experimental (dashed black) and simulated a) acrylate double bond conversion b) rate of polymerization for ITX+NPG photoinitiating system – basic kinetic model (dashed-dotted blue) and model with $R(C=C)_nOO^{\bullet}$ + AH reaction (plain red) (λ_{irr} = 395 nm, 10 mW.cm^{-2}, 0.1 wt% ITX / 1.5×10^{-2} M NPG).

Ketyl radicals as terminating agents – model with termination by ITXH$^{\bullet}$ (ITX+NPG)

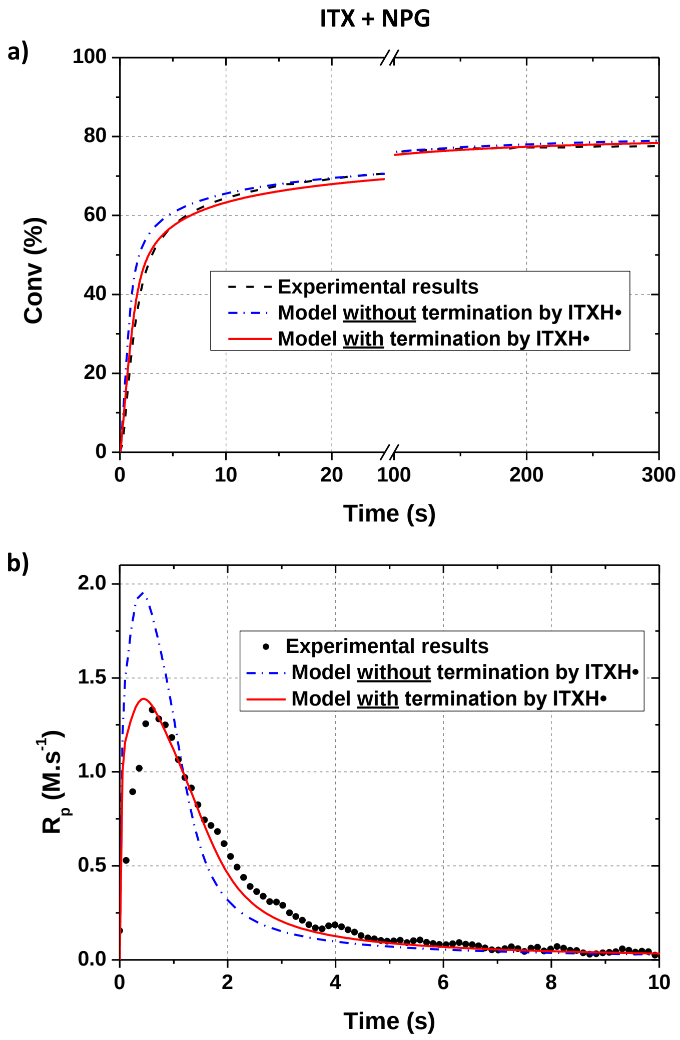
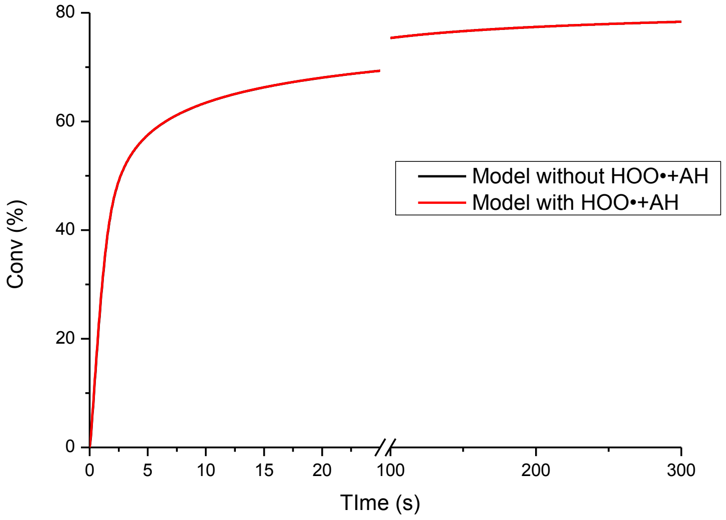


Figure S8: Comparison between experimental (dashed black) and simulated (plain red) a) acrylate double bond conversion b) rate of polymerization for ITX+NPG photoinitiating system – model without (dashed-dotted blue) and with (plain red) termination by ITXH$^{\bullet}$ (λ_{irr} = 395 nm, 10 mW.cm^{-2}, 0.1 wt% ITX / 1.5×10^{-2} M NPG).

Formation of new initiating radicals by reaction of HOO$^{\bullet}$ with AH.



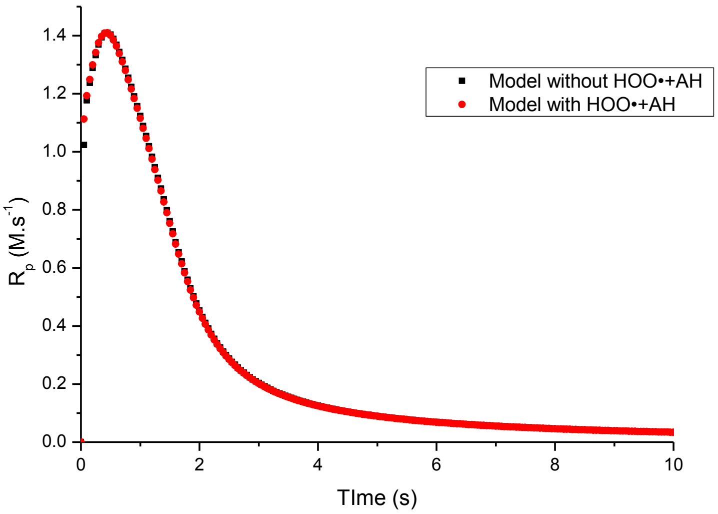


Figure S9: Comparison between the model with and without the reaction of HOO$^{\bullet}$ + AH (λ_{irr} = 395 nm, 10 mW.cm^{-2}, 0.1 wt% ITX / 1.5×10^{-2} M NPG).

Study of the termination pathways

It is possible to simulate the formation of the species terminated by the different pathways (bimolecular termination, PRT by A$^{\bullet}$, PRT by ITXH$^{\bullet}$ or oxygen inhibition) during the photopolymerization process with the following differential equations:

$$\frac{d[\mathrm{bimol}]}{dt} = 2k_{t,b}[R(C{=}C)_n^{\bullet}]^2$$

$$\frac{d[R(C{=}C)_nA]}{dt} = k_{t,PRT}{}^{A^{\bullet}}[A^{\bullet}][R(C{=}C)_n^{\bullet}]$$

$$\frac{d[R(C{=}C)_nITXH]}{dt} = k_{t,PRT}{}^{ITXH^{\bullet}}[ITXH^{\bullet}][R(C{=}C)_n^{\bullet}]$$

$$\frac{d[R(C{=}C)_nOO^{\bullet}]}{dt} = k_{O_2}{}^{R(C=C)_n^{\bullet}}[R(C{=}C)_n^{\bullet}][O_2]$$

[bimol] stands for the concentration of the macroradicals terminated by combination or dismutation, $[R(C{=}C)_nA]$ the concentration of the macroradicals terminated by a PRT reaction with $A^{\bullet}$, $[R(C{=}C)_nITXH]$ the concentration of that terminated with $ITXH^{\bullet}$ and $[R(C{=}C)_nOO^{\bullet}]$ the peroxy radicals derived from the inhibition of the macroradicals by oxygen. At the end of the polymerization, all the remaining macroradicals are considered trapped in the tridimensional matrix by occlusion.

Study of the inhibition reactions

In a similar manner than for the termination reactions, it is possible to determine the concentration of the inhibited species formed throughout the photopolymerization with the following differential equations:

$$\frac{d[TripO_2]}{dt} = k_{O_2}{}^{^3ITX}[^3ITX][O_2]$$

$$\frac{d[AOO^{\bullet}]}{dt} = k_{O_2}{}^{A^{\bullet}}[A^{\bullet}][O_2]$$

$$\frac{d[ITXHOO^{\bullet}]}{dt} = k_{O_2}{}^{ITXH^{\bullet}}[ITXH^{\bullet}][O_2]$$

$$\frac{d[R(C{=}C)_nOO^{\bullet}]}{dt} = k_{O_2}{}^{R(C=C)_n^{\bullet}}[R(C{=}C)_n^{\bullet}][O_2]$$

$TripO_2$ represents the ITX triplet states quenched by O_2, $AOO^{\bullet}$ the peroxy radicals derived from the aminoalkyl ones $A^{\bullet}$, $ITXHOO^{\bullet}$ the $ITXH^{\bullet}$ ketyl radicals having reacted with O_2 (before their dissociation to yield ^0ITX and $HOO^{\bullet}$) and $R(C{=}C)_nOO^{\bullet}$ the peroxy radicals obtained from the macroradicals.

References

[S1] C. N. Bowman and N. A. Peppas, *Macromolecules*, 1991, **24**, 1914-1920.

[S2] M. D. Goodner, H. R. Lee and C. N. Bowman, *Ind. Eng. Chem. Res.*, 1997, **36**, 1247-1252.

[S3] M. D. Goodner and C. N. Bowman, *Chem. Eng. Sci.* 2002, **57**, 887-900.

[S4] T. M. Lovestead, A. K. O'Brien and C. N. Bowman, *J. Photochem. Photobiol. A*, 2003, **159**, 135-143.

[S5] M. D. Goodner and C. N. Bowman, *Macromolecules*, 1999, **32**, 6552-6559.

[S6] A. Ibrahim, V. Maurin, C. Ley, X. Allonas, C. Croutxé-Barghorn and F. Jasinski, *Eur. Polym. J.*, 2012, **48**, 1475-1484.

[S7] J. Christmann, X. Allonas, C. Ley, A. Ibrahim and C. Croutxé-Barghorn, *Macromol. Chem. Phys.*, 2017, **218**, 1600597-1-1600597-10.

[S8] G. Amirzadeh and W. Schnabel, *Makromol. Chem.*, 1981, **182**, 2821-2835.

[S9] C. Ley, J. Christmann, A. Ibrahim, L. H. Di Stefano and X. Allonas, *Beilstein J. Org. Chem.*, 2014, **10**, 936-947.

[S10] V. Charlot, A. Ibrahim, X. Allonas, C. Croutxé-Barghorn and C. Delaite, *Polym. Chem.*, 2014, **5**, 6236-6243.

[S11] K. S. Anseth and C. N. Bowman, *Polym. Reac. Eng.*, 1993, **1**, 499-520.

[S12] K. Taki, Y. Watanabe, H. Ito and M. Ohshima, *Macromolecules*, 2014, **47**, 1906-1913.

[S13] J. Lalevée, B. Graff, X. Allonas and J-P. Fouassier, *J. Phys. Chem. A*, 2007, **111**, 6991-6998.

[S14] M. Buback, *Makromol. Chem.*, 1990, **191**, 1575-1587.