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Julien Christmann, Ahmad Ibrahim, Vincent Charlot, Celine Croutxé-Barghorn, Christian Ley, et al.. Elucidation of the Key Role of $[\text{Ru}(\text{bpy})_3]^{2+}$ in Photocatalyzed RAFT Polymerization. ChemPhysChem, 2016, 17 (15), pp.2309-2314. 10.1002/cphc.201600034 . hal-03031035

HAL Id: hal-03031035

<https://uca.hal.science/hal-03031035v1>

Submitted on 30 Nov 2020

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Elucidation of the Key-Role of $[\text{Ru}(\text{bpy})_3]^{2+}$ in Photocatalyzed RAFT Polymerization

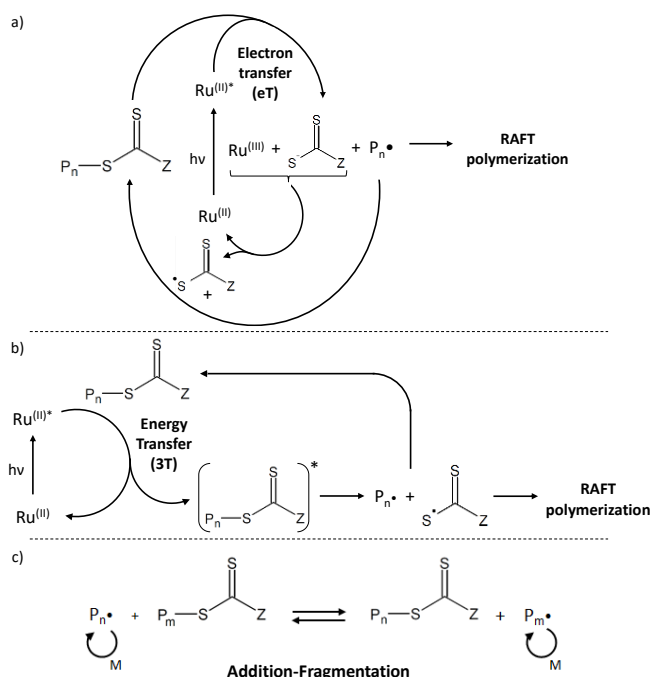
J. Christmann, A. Ibrahim, X. Allonas*, V. Charlot, C. Croutxé-Barghorn, C. Ley

Abstract: The photocatalysis reaction using $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ was studied on the example of visible light sensitized Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization. Although both photoinduced electron and energy transfer mechanisms are able to describe this interaction, no definitive experimental proof has been evidenced so far. This paper investigates the actual mechanism governing this reaction. A set of RAFT agents was selected, their redox potentials measured by cyclic voltammetry and relaxed triplet energies calculated by Quantum Mechanics. Gibbs free-energy values were calculated for both electron and energy transfer mechanisms. Quenching rate constants were determined by Laser Flash Photolysis. The results undoubtedly evidence the involvement of a photoinduced energy transfer reaction. Controlled photopolymerization experiments are discussed in light of the primary photochemical process and photodissociation ability of RAFT agent triplet states.

Organometallic complexes, typified by $[\text{Ru}^{\text{II}}(\text{bpy})_3]\text{Cl}_2$ (bpy = 2,2'-bipyridine), are well-known compounds since the 1970's. They exhibit interesting photochemical properties, such as absorption in the visible region and photoreaction through photoinduced single-electron oxidation or reduction.^[1-5] However, since these pioneering works, few studies have been reported until 2008. From this date, several groups started to exploit the photocatalytic ability of such complexes for a broad range of visible light induced organic reactions under mild conditions: alkylation, dehalogenation, cyclization, cycloaddition...^[6-15] Photoinduced electron transfer (PeT) has been proposed to explain most of these reactions while triplet energy transfer (P3T) has only scarcely been reported to be involved.^[14-15] In parallel, groups have begun to use organometallic complexes to initiate Free Radical Photopolymerization (FRP).^[16-17] One of its major limitations is a lack of control of the macromolecular mass and chain distribution due to transfer and termination reactions. Controlled photopolymerization reactions have been subsequently proposed.^[18-21] Among them, Reversible Addition-Fragmentation chain Transfer (RAFT) photopolymerization have been initially based on the dissociation of RAFT agents under UV light.^[22-25] Generated radicals further initiate and control the radical polymerization. Detrimental UV lamps were afterwards replaced by visible light sources thank to the introduction of organometallic complexes.^[26-30] Excited complexes act then as photosensitizers for the dissociation of the RAFT agents. Most

recent studies have reported direct dissociation of RAFT molecules under blue and green light irradiation.^[31-33] Although that the key-role of organometallic complexes has been highlighted in photosensitized systems, no detailed investigation was made to clarify the mechanism.^[26-30] The aim of this paper is to understand the photochemical mechanism implied in RAFT polymerization photocatalyzed by $[\text{Ru}^{\text{II}}(\text{bpy})_3]\text{Cl}_2$. Photopolymerization experiments of methyl acrylate will be discussed in the light of the involved mechanism.

As mentioned above, two different mechanisms can be proposed to describe the photocatalysis of the RAFT process by $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$: photoinduced electron and energy transfer. For electron transfer, initiating and transfer radicals are separately produced, as proposed in Scheme 1a.^[26] Initiating radicals are generated by the bimolecular electron transfer from the excited Ru complex to a RAFT (macro)molecule. Transfer species result from the bimolecular reaction of the oxidized Ru complex with the reduced form of the RAFT agent. However, the involvement of two consecutive bimolecular reactions tends to lower the probability of the radical production. In energy transfer mechanism, both radicals are produced through a dissociation of the C – S bond of the excited RAFT (macro)molecule (Scheme 1 b). In both cases, addition-fragmentation controls the macromolecular mass distribution (Scheme 1 c).



Scheme 1. a) Photoinduced electron transfer (PeT) mechanism (adapted from [26]). b) Triplet photoinduced energy transfer (P3T) mechanism c) Reversible addition-fragmentation transfer mechanism.

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In order to elucidate the actual photochemical mechanism, eight commercial RAFT agents were selected. Structures of $[\text{Ru}^{\text{II}}(\text{bpy})_3]\text{Cl}_2$ (1) and the RAFT agents (2 – 9) are shown in Figure 1.

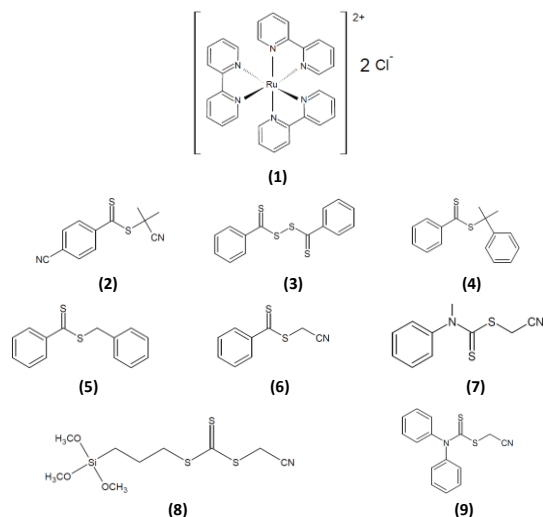


Figure 1. Structure of the compounds studied: $[\text{Ru}^{\text{II}}(\text{bpy})_3]\text{Cl}_2$ (1) and RAFT agents (2 – 9).

The Gibbs free-energy change of the photoinduced electron transfer reaction ΔG_{PET} between an electron donor D and an acceptor A is calculated according to the Rehm-Weller equation:^[34]

$$\Delta G_{\text{PET}} = E_{\text{ox}}(D) - E_{\text{red}}(A) - E^* + C \quad \text{Eq. (1)}$$

E_{ox} and E_{red} refer to oxidation and reduction potentials, respectively. E^* stands for the triplet energy of Ru complex and C

is a Coulombic term which could be neglected in polar solvents. Relaxed triplet energies of the RAFT agents (2 – 9) were calculated by Quantum Mechanics (QM) at the Density Functional Theory (DFT) level. The possibility of an energy transfer is estimated through calculation of the Gibbs free-energy variation ΔG_{P3T} .

$$\Delta G_{\text{P3T}} = E^*(A) - E^*(D) \quad \text{Eq. (2)}$$

$E^*(A)$ and $E^*(D)$ are the triplet state energies of the Acceptor and Donor, respectively.

Quenching rate constants (k_q) of (1) by the RAFT agents were deduced from Stern-Volmer plots, using Laser Flash Photolysis (LFP) experiments.^[35] All these data are collected into Table 1.

Electron transfer reaction

$\log(k_q)$ is plotted as a function of ΔG_{PET} with (1) taken either as an oxidant or a reductant (Figure 2). With (1) as an oxidant, no clear relationship appears between $\log(k_q)$ and ΔG_{PET} . By contrast, the k_q values increase with increasing ΔG_{PET} values.

When (1) acts as a reductant, experimental values would better follow a Rehm-Weller behaviour. However, high values of k_q , as found for (4) to (7) are not consistent with the corresponding positive values of Gibbs free-energy. An electron transfer mechanism thus appears unlikely. In order to confirm this contention, attempt was made to detect the formation of oxidized Ru complex by laser flash photolysis. First, the transient absorption spectrum of (1) was recorded in acetonitrile after laser flash (Figure 3a). As known, the triplet state of Ru complex absorbs at 360 nm, and the photobleaching of the ground state appears around 450 nm. In the presence of iodonium salt (Irgacure 250, I250) as strong oxidant (Figure 3b), a new absorption band appears at 420 nm which is attributed to $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$.^[2] The ground state of (1) at 440 nm also exhibits a partial photobleaching as a consequence of the long-lived oxidized form of Ru complex.

Table 1: Redox potentials, relaxed triplet energy, corresponding Gibbs free-energies and quenching rate constant of the studied compounds.

Compound	$E_{\text{ox}} / \text{SCE} (\text{V})^{[a]}$	$\Delta G_{\text{PET}}^{\text{Ru=ox}} (\text{kJ}\cdot\text{mol}^{-1})$	$E_{\text{red}} / \text{SCE} (\text{V})^{[a]}$	$\Delta G_{\text{PET}}^{\text{Ru=red}} (\text{kJ}\cdot\text{mol}^{-1})$	$E_{\text{T}}^{\text{rel}} (\text{kJ}\cdot\text{mol}^{-1})$	$\Delta G_{\text{P3T}} (\text{kJ}\cdot\text{mol}^{-1})$	$k_q (\text{M}^{-1}\cdot\text{s}^{-1})$
1	1.22	-	- 1.37	-	205.5 ^[b]	-	-
2	> 2	> 119.6	- 0.83	- 7.7	137.2	- 68.3	7.2·10 ⁹
3	1.26	48.2	- 0.74	- 16.4	≥ 86.1	- 119.4	5.6·10 ⁹
4	1.44	65.6	- 1.25	32.8	120.1	- 85.4	3.4·10 ⁹
5	1.56	77.2	- 1.27	34.7	159.2	- 46.3	2.9·10 ⁹
6	> 2	> 119.6	- 1.12	20.3	162.7	- 42.8	2.4·10 ⁹
7	1.54	75.2	< - 2	> 105.2	≥ 165.1	- 40.4	1.6·10 ⁸
8	0.85	8.7	- 1.50	56.9	187.8	- 17.7	8.8·10 ⁶
9	0.59	-16.4	- 1.77	83.0	201.2	- 4.3	5.4·10 ⁶

[a] "> 2" or "< - 2" refers to values out of the analysis range offered by our setup. [b] From [1-2].

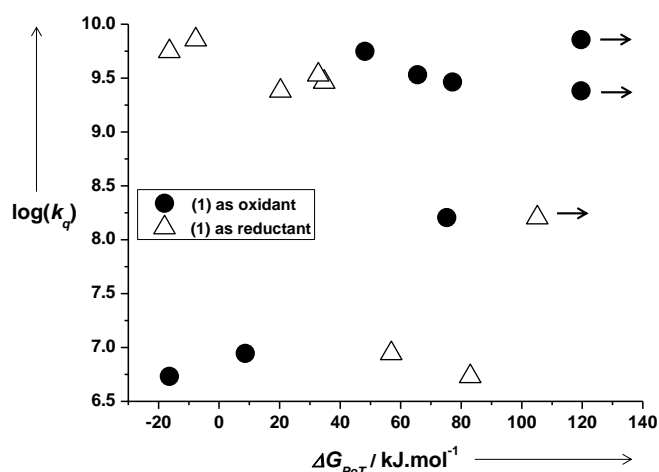


Figure 2. Plot of $\log(k_q)$ as a function of ΔG_{PeT} for (1) as an oxidant (●) and a reductant (▲).

However, when replacing the iodonium salt by RAFT agents, no such band appears at 420 nm (Figure 3c, also see SI for other RAFT agents), evidencing that no oxidation of (1) occurs. Moreover, transient kinetics at 440nm, corresponding to the Ru ground state photobleaching, clearly shows that no long-lived transient is formed after triplet quenching by the RAFT agents. It should be noticed that direct excitation of RAFT agents hardly leads to detectable transient. All these results evidence that photoinduced electron transfer is not involved. This, in turn, suggests that energy transfer would be favoured in this reaction.

Energy transfer reaction

The lack of experimental evidence of electron transfer in laser flash photolysis experiments suggests that energy transfer is involved. In order to evaluate the feasibility of such energy transfer reaction from the triplet excited Ru complex to the RAFT agents, the triplet state energy of these latter were calculated using density functional theory method (Table 1). All relaxed triplet energies E_T^{rel} of the RAFT agents were found to be lower than that of (1). This enables exergonic energy transfer reaction to occur. A plot of $\log(k_q)$ as a function of ΔG_{P3T} highlights the monotonous change in the rate constant with the free energy of the reaction, a plateau value close to the diffusion limit being found for (3). Therefore triplet energy transfer clearly explains the sensitization reaction of RAFT agents by Ru complex. The k_q values can be successfully fitted by the Balzani's model, assuming $k_{diff} = k_{diff} \approx 2.10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ in MeCN (Figure 4):^[36]

$$k_q = \frac{k_{diff}}{1 + \exp\left(\frac{\Delta G_{P3T}}{RT}\right) + \frac{k_{-diff}}{k_{en}}} \text{ with } k_{en} = k_{en}^0 \exp\left(\frac{-\Delta G_{P3T}^\ddagger}{RT}\right) \quad \text{Eq. (3)}$$

$$\Delta G_{P3T}^\ddagger = \Delta G_{P3T} + \frac{\Delta G_{P3T}^\ddagger(0)}{\ln(2)} \ln \left[1 + \exp\left(\frac{-\Delta G_{P3T} \ln(2)}{\Delta G_{P3T}^\ddagger(0)}\right) \right]$$

$\Delta G_{P3T}^\ddagger(0)$ represents the activation free energy when $\Delta G_{P3T} = 0$ and is related to the reorganization energy of the reactants after

the reaction. k_{en}^0 is the pre-exponential factor of the rate constant, i.e. when $\Delta G_{P3T}^\ddagger = 0$.

Values of $24.4 \text{ kJ} \cdot \text{mol}^{-1}$ and $3.1 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ were respectively found for $\Delta G_{P3T}^\ddagger(0)$ and k_{en}^0 . The high value of k_{en}^0 simply indicates that the energy transfer preexponential factor is higher than the diffusion rate constant.

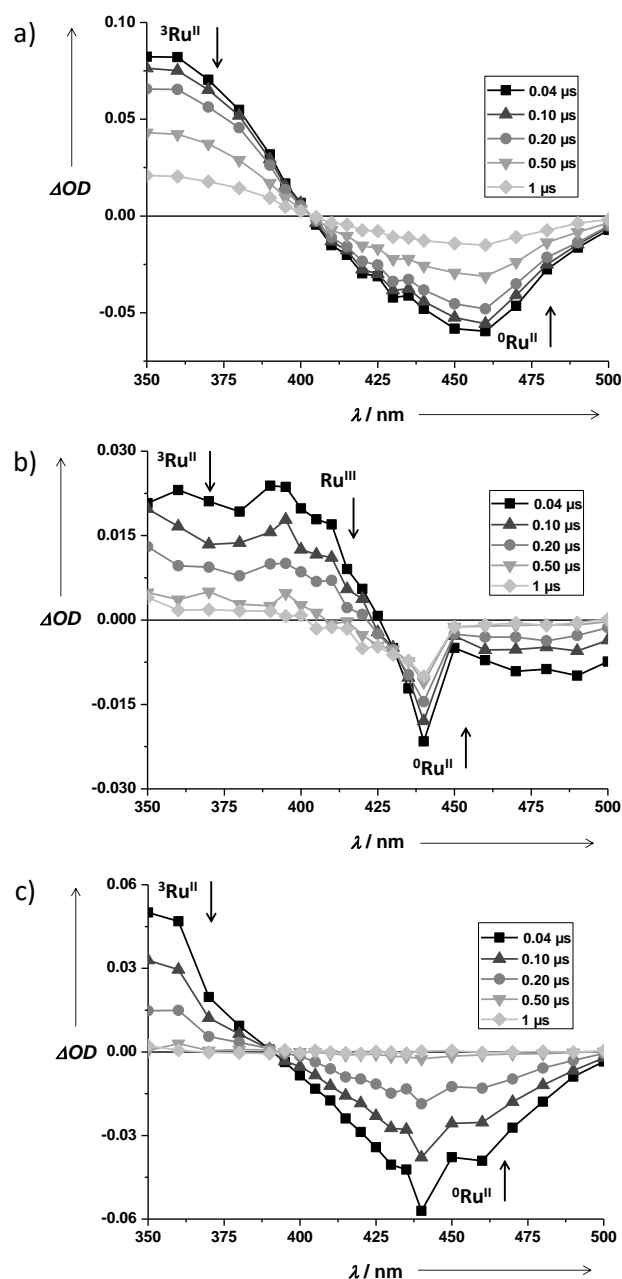


Figure 3. Transient absorption spectrum in MeCN of a) $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$. b) $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+} + \text{I}250$. c) $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+} + (5)$.

Table 2: Conversions, mean-average molecular mass, polydispersity index of poly(methylacrylate) after 10 and 40 min irradiation, bond-dissociation and relaxed triplet energies of RAFT agents and associated dissociation free energy from their triplet state.

Compound	Conv (%) – 10 / 40 min	\bar{M}_n (g.mol ⁻¹) – 10 / 40 min	<i>PDI</i> – 10 / 40 min	<i>BDE</i> (kJ.mol ⁻¹)	E_T^{rel} (kJ.mol ⁻¹)	ΔG_{diss} (kJ.mol ⁻¹)
2	≈ 0 / 0	/	/	143.0	137.2	5.8
3	≈ 0 / 0	/	/	90.0	≥ 86.1	3.9
4	≈ 0 / 0	/	/	140.9	120.1	20.8
5	≈ 0 / 0	/	/	179.8	159.2	20.7
6	≈ 0 / 0	/	/	186.5	162.7	23.8
7	5.8 / 17.3	24,000 / 16,000	1.93 / 1.92	170.7	≥ 165.1	5.6
8 ^[a]	/	/	/	191.2	187.8	3.5
9	30.2 / 52.0	10,600 / 10,000	1.85 / 1.92	173.0	201.2	-28.2

[a] No experiment was possible with this compound.

The relatively high value of $\Delta G_{P3T}^\ddagger(0)$ highlights a large molecular reorganization of the compounds after the reaction. As the structure of the Ru complex is quite rigid, this would indicate that the triplet states of the RAFT agents are distorted with respect to their ground states.^[37-39] This may somehow be related to a predissociative triplet state.

Therefore, energy transfer process is in agreement with the transient absorption experiments described above.

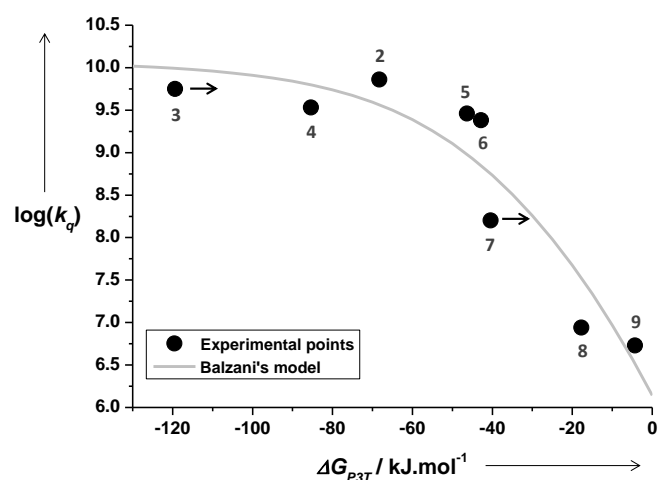


Figure 4. Plot of $\log(k_q)$ as a function of ΔG_{P3T} and corresponding fit with Balzani's energy transfer model.

Photosensitized controlled polymerization

Polymerization of poly(methylacrylate) (PMA) was performed in presence of $[\text{Ru}^{\text{II}}(\text{bpy})_3]\text{Cl}_2$ and the different RAFT agents with a 455 nm LED in tetrahydrofuran. Polymer conversions were measured for two different irradiation times (10 and 40 min) by FTIR spectroscopy. Mean-average molecular mass (\bar{M}_n) and PolyDispersity Index (*PDI*) of the obtained polymers were characterized by steric exclusion chromatography (Table 2 and

Figure 5). No inhibition time could be noticed for these experiments performed under Ar atmosphere.

As seen on Figure 5, only two RAFT agents lead to efficient polymerization (7 and 9). \bar{M}_n are about 10,000-16,000 g.mol⁻¹ and *PDI* 1.9. The effectiveness of the polymerization is partly governed by the dissociation free energy (ΔG_{diss}) of the RAFT agent:

$$\Delta G_{diss} = BDE - E_T^{rel} \quad \text{Eq. 4}$$

BDE stands for the bond dissociation energy of the RAFT agent as estimated by DFT. These values are collected in Table 2. Figure 5 shows that there is a clear relationship between the monomer conversion and the photodissociation reaction.

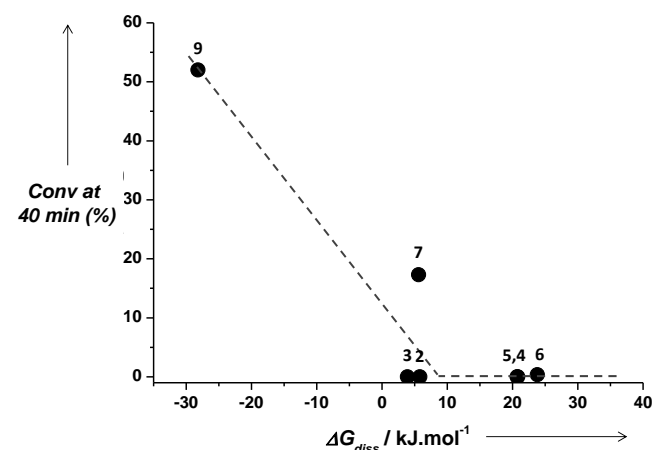


Figure 5. Plot of conv at 40 min (%) as a function of ΔG_{diss} .

No photosensitized bond-breaking reaction is expected for compounds (4), (5) and (6) due to unfavorable thermodynamics ($BDE > E_T^{rel}$). For compounds (2), (3) and (7), ΔG_{diss} values are close to zero and consequently the conversion are low. Differences in conversion values merely arise from differences in

chemical structures. A detailed investigation of these effects is out of the scope of this paper. By contrast, the thermodynamics of (9) is highly favorable. Consequently, it leads to the best conversion of MA. It can be concluded that the triplet state of (9) is sufficiently energetic to dissociate and to create the initiating radicals. SEC results confirm that a polymer was obtained which exhibits $PDI = 1.9$, corresponding to a well-controlled polymerization for such a free radical process.

In conclusion, the key role of $[Ru^{II}(bpy)_3]Cl_2$ as photocatalyst for the RAFT photopolymerization of methyl acrylate has been elucidated. Mechanistic studies by LFP and calculations of ΔG changes indicated that photoinduced electron transfer (PeT) is disfavored. On the contrary, triplet photoinduced energy transfer (P3T) mechanism appears to match quite well the experimental data using the computed triplet energies of the RAFT agents. Balzani's model has been successfully applied to the experimental data. In addition, photosensitized controlled polymerization of MA has also emphasized the importance of the bond dissociation energy (BDE) of the RAFT agent. The better understanding of the photochemical mechanisms involved will offer new perspectives for the development of controlled radical photopolymerization photosensitized with visible light.

Methods

Complete name, origin and purity of the chemical compounds are detailed in the SI. Redox potentials were determined by cyclic voltammetry, as described elsewhere.^[40] Quantum mechanical calculations were performed at (U)B3LYP/6-31G* (for geometry optimization) and (U)B3LYP/6-311++G(d,p) (for single point calculations) levels, using Gaussian 03. Description of the complete methodology is presented in the SI. Description of the setup and the experimental conditions for laser flash photolysis experiments is also given in the SI.

A typical formulation for the polymerization of MA was composed of 6.7 g of MA (3.15 mol.L^{-1}), ruthenium complex ($0.04 \text{ wt\%} - 0.13 \text{ mmol.L}^{-1}$) and RAFT agent (0.4 wt\%), completed to 25 mL with tetrahydrofuran (THF). Irradiation was ensured by a 455-nm blue LED (Phoseon – Firejet FJ200) set at 8W and located at 5 cm from the cuvette containing the formulation. Monomer conversion was studied with a Real-Time Fourier Transform InfraRed (RT-FTIR) spectrometer (Brucker Optics – Vertex 70) equipped with a DTGS detector and used in stationary mode. The conversion was determined by the decrease of the area of the C=C vibration band of MA in near-infrared ($4,739 \text{ cm}^{-1}$) and calculated with the following formula:

$$\text{Conv (\%)} = \frac{(A_0 - A_t)}{A_0} \times 100 \quad \text{Eq. 5}$$

where A_0 and A_t represent respectively the absorption band area before exposure and at a time t . Complementary details are set in the SI.

Mean-average molecular mass (\bar{M}_n) and PolyDispersity Index (PDI) of the formed PMA were determined using Size Exclusion Chromatography (SEC). Analyses were performed on a Shimadzu LC-20AD liquid chromatograph. Molecular masses are given in polystyrene equivalents. Experimental conditions are further described in the SI.

Keywords: photocatalysis • energy transfer • computational chemistry • RAFT photopolymerization

Acknowledgements: ANR and Mäder are fully acknowledged for financial support of the DeepCure project #ANR-13-CHIN-0004-01.

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