

# TR ESR Study of Elementary Reactions of Photoinitiation and Termination

*Elena Sartori*

*Chemistry Department, Columbia University, New York, NY, USA*

*Igor V. Khudyakov*

*Bomar Specialties, Torrington, CT, USA*

*Nicholas J. Turro\**

*Chemistry Department, Columbia University, New York, NY, USA*

## Abstract

Results of a time-resolved (TR) ESR study of direct and sensitized photoinitiation of polymerization of acrylates are presented. TR ESR allows unequivocal identification of primary and secondary transient radicals -spin adducts- that are formed during photoinitiation. A TR ESR study of termination of free radicals of photoinitiators with stable nitroxyls and binitroxyls is discussed.

## Introduction

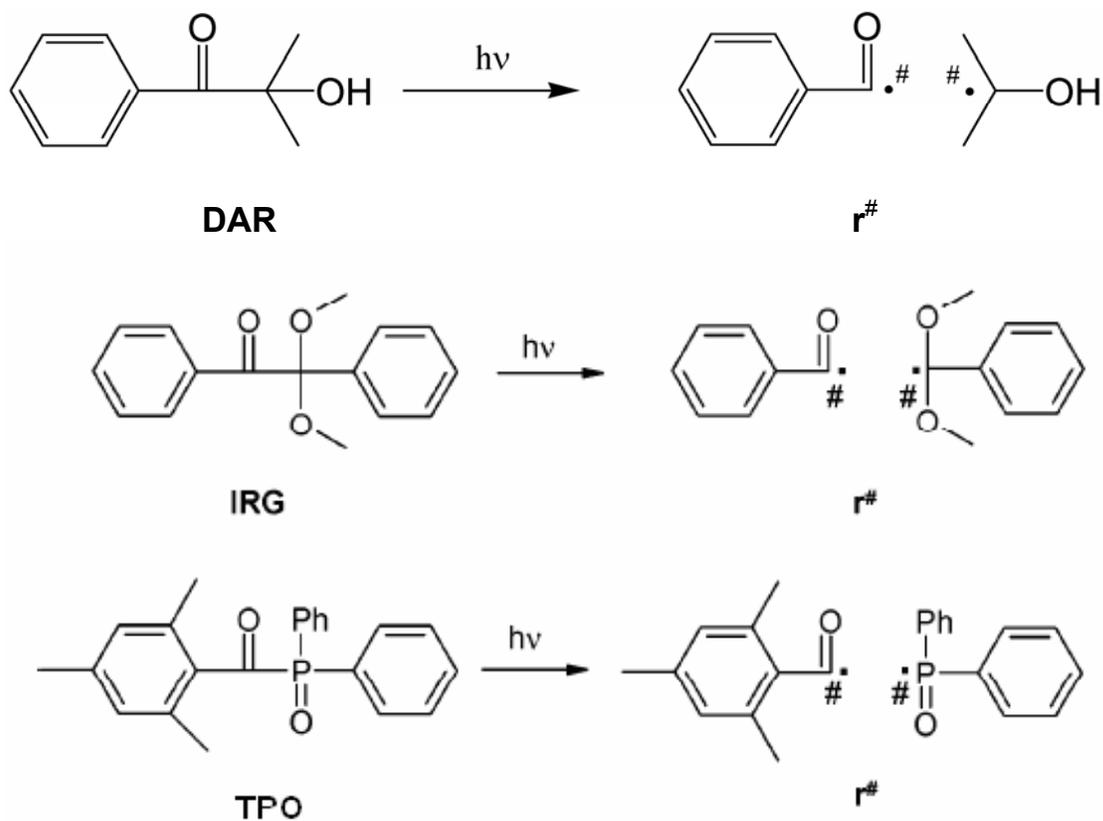
Flash photolysis of photoinitiators (PIs) of free radical polymerization in the cavity of ESR spectrometer is often accompanied by chemically induced dynamic electron polarization (CIDEP), i.e., by formation of radicals with non-Boltzmann population of electron Zeeman levels.<sup>1,2</sup> CIDEP manifests itself in enhanced absorption or emission of all or of certain components in ESR spectra of photogenerated free radicals. Radicals, which manifest CIDEP, are often called polarized. The main mechanisms leading to CIDEP in photoinduced reactions are well established and have been investigated both theoretically and experimentally.<sup>1,2</sup>

Analysis of CIDEP pattern with time-resolved (TR) ESR spectra allows for a solid conclusion on spin multiplicity of molecular precursors of polarized free radicals (a singlet or a triplet excited molecules) and the tracking of fast reactions of polarized radicals leading to secondary radicals. Thus, TR ESR is a convenient method in mechanistic photochemistry and free radical chemistry. In this work, we used a common continuous wave (cw) TR ESR device. It consists of nanosecond laser flash photolysis ( $\lambda_{\text{ex}}$  308 or 355 nm) with a detection of transients by their ESR spectra with X-band ESR spectrometer in the direct detection mode (no field modulation).<sup>3-5</sup> All experiments were performed at room temperature.

## Photoinitiation

Many research groups, including Columbia Photochemistry Group, have observed TR ESR spectra under photolysis of commercial PIs Darocur 1173 (**DAR**), Irgacures, and in particular Irgacure 651 (**IRG**), *mono*-phosphine oxide (Lucerin TPO or **TPO** here for brevity), *bis*-phosphine oxide (**BAPO**). Analysis of ESR spectra of formed primary radicals and their spin-adducts allows determination of radical structure. Computer simulation with user-friendly software is used with to elucidate radical structure.

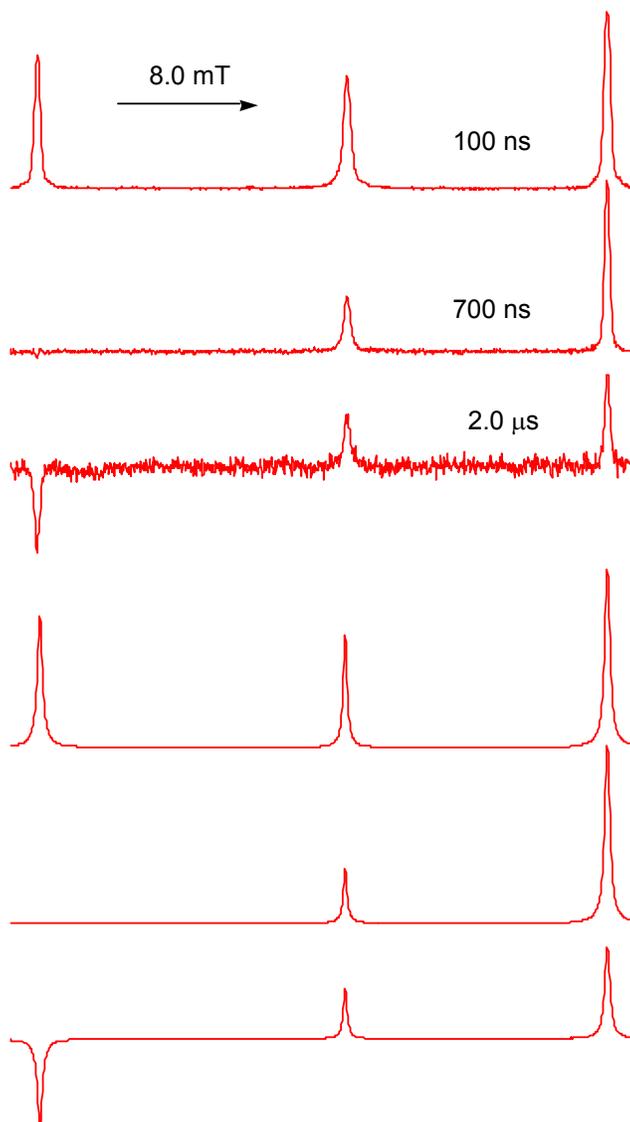
Reactions below represent photolysis of **DAR**, **IRG** and **TPO** leading to polarized free radicals of PIs:



**Scheme 1.** Photolysis of these PIs occurs via triplet state and leads to polarized reactive free radicals.

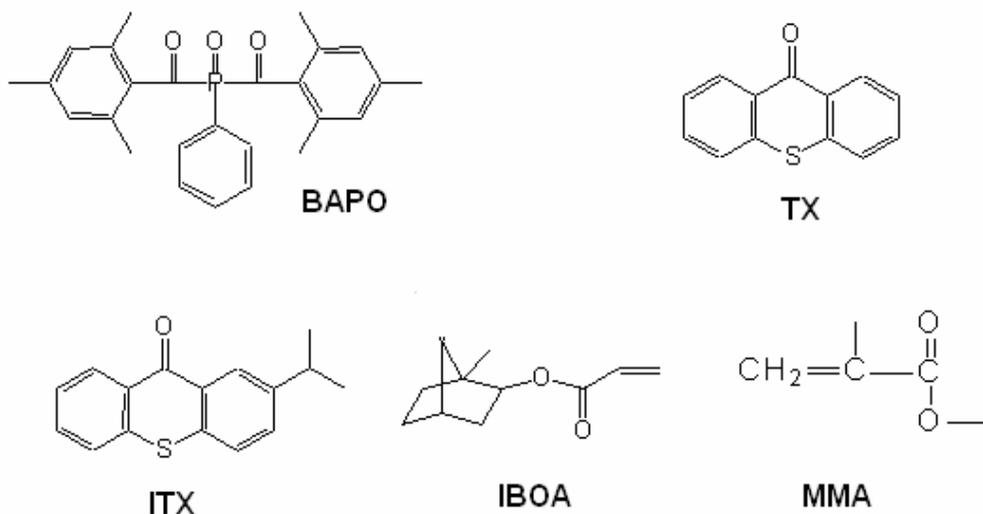
The superscript  $\#$  is used throughout this report to indicate spin polarization, a term applied to situations for which a paramagnetic species possesses a population of spin states that is different from the Boltzmann distribution at the temperature of the experiment. Polarization disappears during radical paramagnetic relaxation time, usually in the microsecond time scale.

Reactive radicals  $r$  of PI initiate polymerization. Figure 1 below demonstrates TR ESR spectra obtained under photolysis of **TPO**:



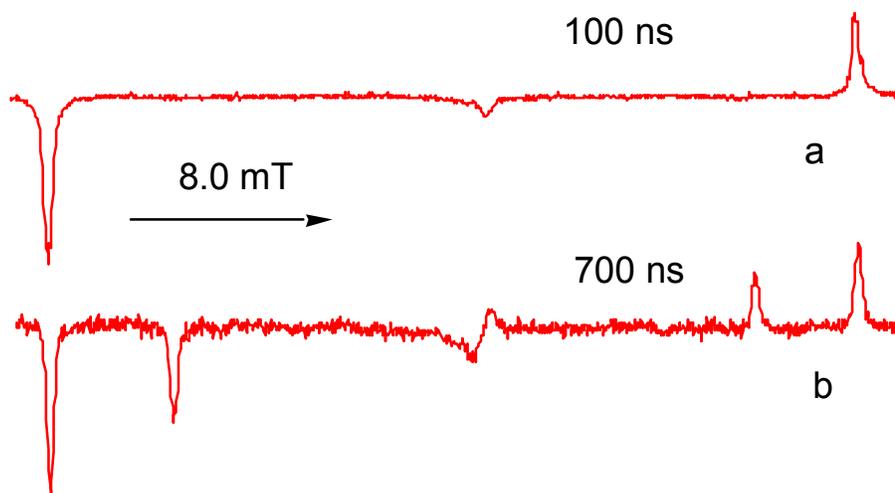
**Figure 1.** TR ESR spectra of **TPO** in ethyl acetate were taken at different observation times after a laser pulse. The three computer-simulated spectra are presented below the three experimental spectra. Two outmost components correspond to a large hyperfine coupling on P-atom. The signal in the center of the spectrum corresponds to 2,4,6-trimethylbenzoyl radical (an envelope of small hyperfine (HF) coupling).<sup>5,6</sup>

Chemical structures of other compounds used in this work, viz. **BAPO**, photosensitizers thioxanthene-9-one (**TX**) and 2-isopropyl thioxanthene-9-one (**ITX**), monomers isobornyl acrylate (**IBOA**) and methyl methacrylate (**MMA**) are presented in Scheme 2.



**Scheme 2.** Chemical structures and designations of reagents used in this work.

Energies of triplet states of sensitizers **TX** (**ITX**) and of PIs **TPO** (**BAPO**) are close to each other ( $\sim 260$  kJ/mol), allowing for slightly exothermic or thermoneutral T-T energy transfer from sensitizer to PI.<sup>6</sup> Direct photolysis of phosphine oxides results in a well-documented initial strong *absorptive* (A) pattern of ESR spectra, cf. Figure 1 and Scheme 4 below. Sensitized by **TX** or **ITX** photolysis of phosphine oxides leads evidently to the same radicals, but an initial polarization pattern is quite different, namely *emission/absorption* (E/A) pattern, cf. Figure 2.



**Figure 2.** TR ESR spectra in ethyl acetate of: (a) **TPO** in the presence of **TX**; (b) a mixture of **TPO** and **BAPO** in the presence of **ITX**. Laser light was absorbed predominantly by sensitizers.<sup>6</sup>

Thus, an observation of TR ESR spectra patterns allows the determination of the reaction pathway leading to the same radicals. In the case study, it is direct vs. sensitized photolysis.

TR ESR spectrum of **DAR** is presented below in Scheme 5.

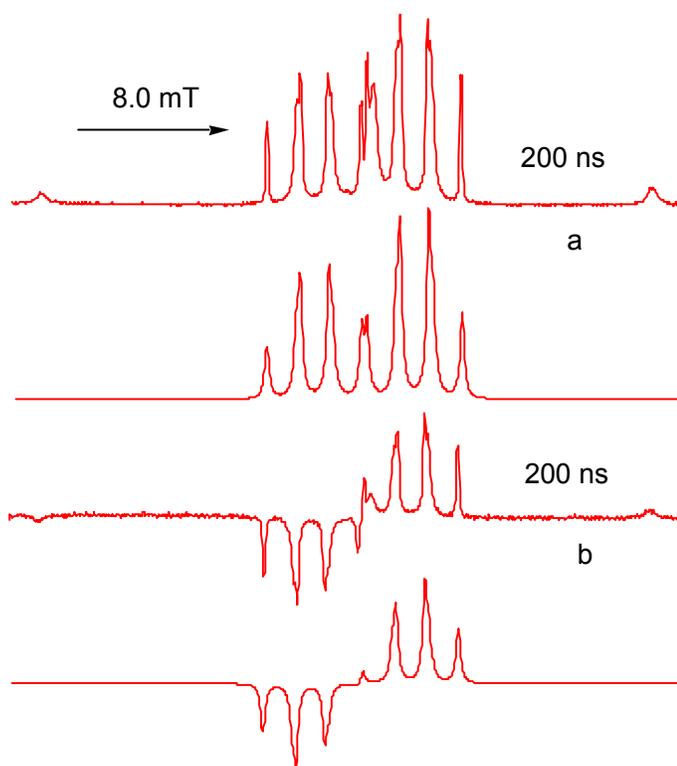
### Addition

Addition of a free radical of initiator **r** to a monomer (oligomer) **M** is often considered as a part of initiation. In our experiments **r<sup>#</sup>** was polarized, as well as the secondary radical:



It will be demonstrated in this report that in the fast reactions of polarized radicals, polarization is preserved and is transferred into secondary radicals or adducts. As examples of the addition study, we will consider the reaction of **r** of **TPO** with **IBOA** and with **MMA**.

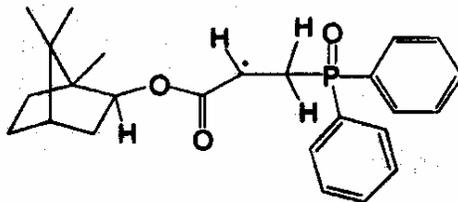
TR ESR spectra of PIs in the presence of **IBOA** are presented in Figure 3:



**Figure 3.** TR ESR spectra in ethyl acetate of: (a) **TPO** in the presence of **IBOA**; (b) **BAPO** in the presence of **TX** and **IBOA**. In the later case laser light was absorbed mainly by triplet sensitizers. Computer-simulated spectra are shown below each

experimental spectrum.<sup>6</sup>

The observed spectra (Figure 3) consist mainly of polarized signals of spin-adducts of phosphinoyl radical and acrylate of the following structure:

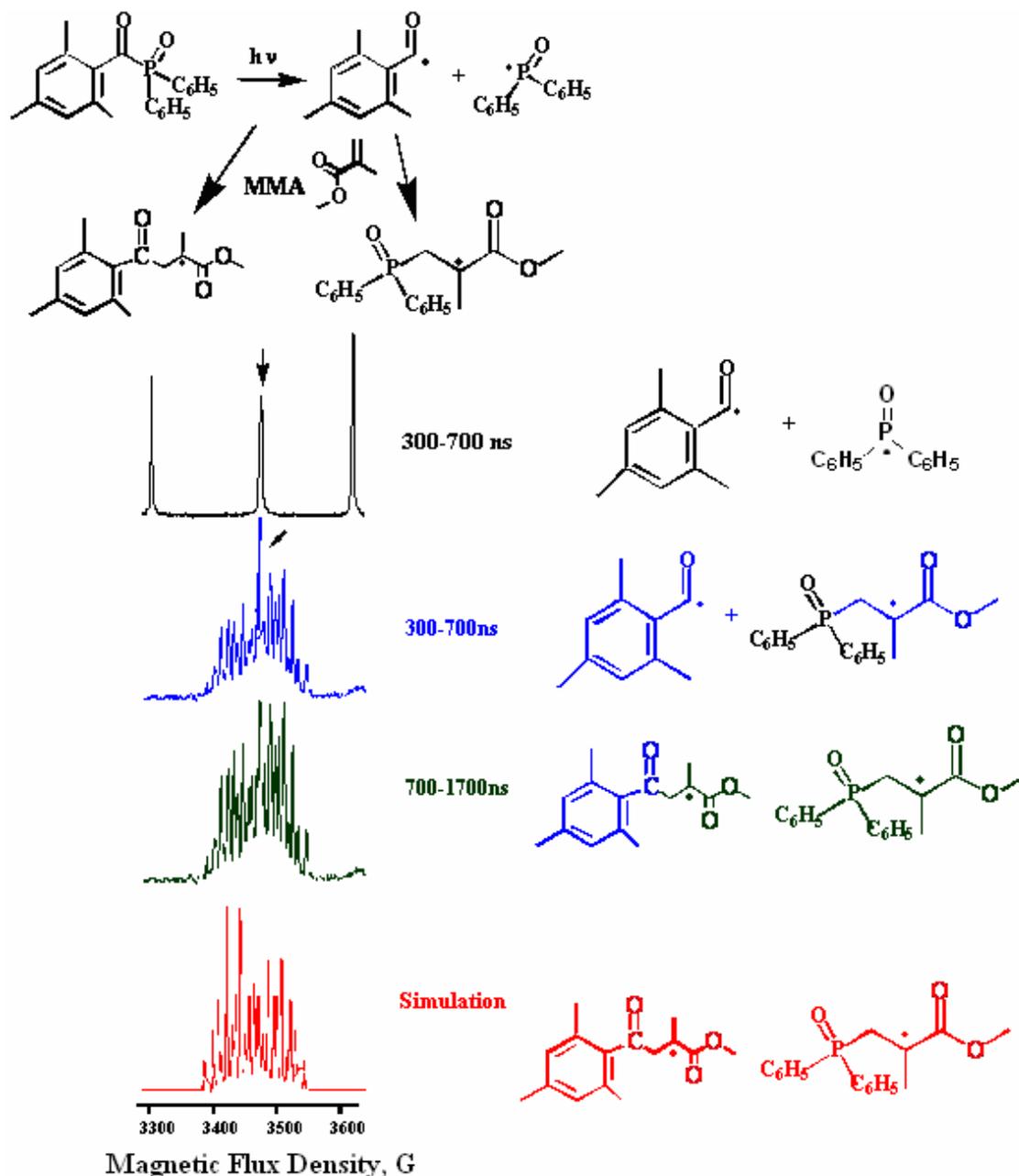


**Scheme 3.** The structure of the main product of addition of phosphinoyl radical to **IBOA**. It is a so-called “head-to-tail” adduct, where **r** adds to CH<sub>2</sub>-group (“tail”).

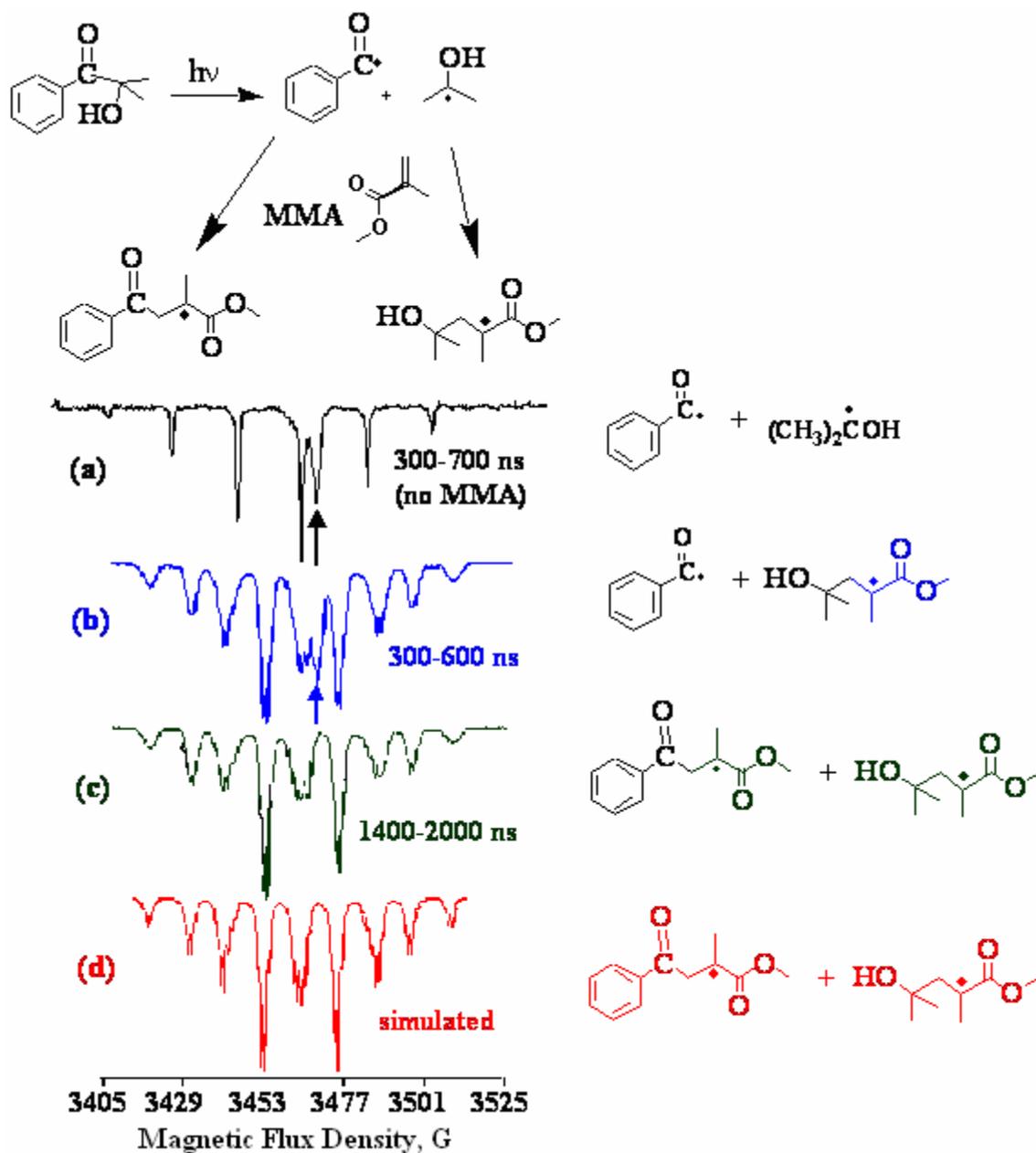
(Substituted) benzoyl radicals are known to be much less reactive than phosphinoyl radicals in addition to acrylates, and benzoyl radicals persist contributing to the center of the experimental spectra (Figure 3); cf. additional comments below.

The spectra presented in Figures 1-3 demonstrate that polarization pattern is preserved during a fast addition of radicals to a monomer. Absorptive (A) polarization observed under direct photolysis of PIs (Figure 1, Scheme 4 below) results in A-pattern of spectrum of the spin-adduct (Figure 3a), and the E/A-pattern observed under sensitized photolysis (Figure 2) results in an E/A-pattern of spectrum of the spin adduct (Figure 3b). Thus, TR ESR allows the establishment of not only the origin and structure of free radicals, but their reactions as well.

Schemes 4 and 5 present two other cases of addition of **r**, this time to the monomer **MMA**, which is very important in industry:



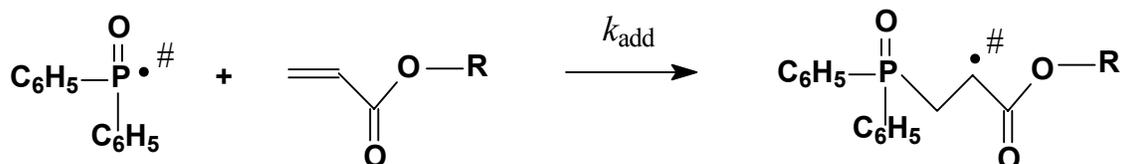
**Scheme 4.** TR ESR study of addition of  $r$  of TPO to MMA in ethyl acetate. Arrows at the spectra point to a signal of substituted benzoyl radical. The top spectrum was obtained under photolysis of TPO only. The second and the third spectra from the top were taken in the presence of MMA. The spectra correspond to adducts of both  $r^\#$  of TPO to MMA. Both adducts are “head-to-tail”. All radicals are polarized; sign  $\#$  is not shown in this Scheme and in Scheme 5 below.



**Scheme 5.** TR ESR study of addition of  $r$  of DAR to MMA in ethyl acetate. Arrows at the spectra point to a signal of benzoyl radical. The top spectrum was obtained under photolysis of DAR only. Two spectra below were taken in the presence of MMA. They correspond to adducts of both  $r^\#$  of DAR to MMA. Both adducts are “head-to-tail”.

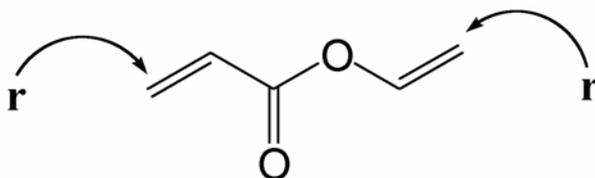
The data shown in of Schemes 3 and 4 confirm that addition of (substituted) benzoyl radicals is slower than that of counter radicals, and therefore the benzoyl adducts have weak signals in the TR ESR spectra.

We conclude that the dominant process under photoinitiation of polymerization of (meth)acrylates by **TPO** is a “head-to-tail” addition of phosphinoyl radical to a double bond:



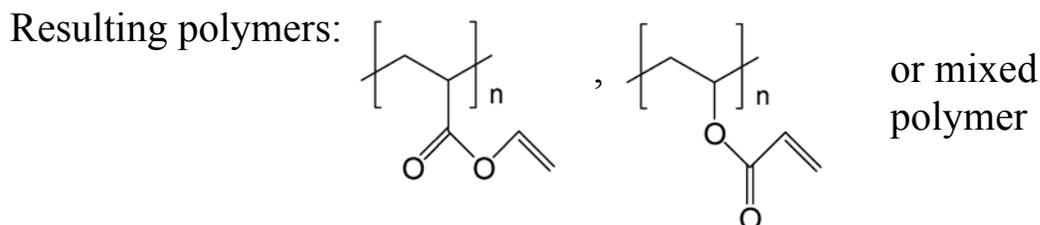
**Scheme 6.** Reaction of phosphinoyl radical with acrylate.

Vinyl acrylate is an intriguing compound capable of self-initiation under UV-irradiation.<sup>7,8</sup> Photopolymerization of vinyl acrylate proceeds faster when PI is added, the other conditions being the same. The question is which double bond is attacked by **r** of PI:



**Scheme 7.** Cf. the text.

Different reactivity of double bonds towards free radicals will lead to either polyacrylate or to poly(1-acryloyloxyethylene), or to a mixed polymer if reactivity of both double bonds are comparable (Scheme 8):



**Scheme 8.** Structures of polymers that can be formed under free-radical polymerization of vinyl acrylate.

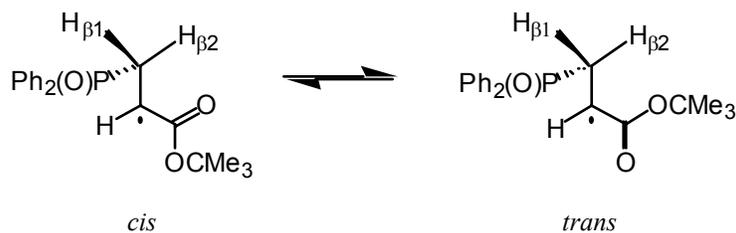
One can formally expect the formation of total *eight adducts* under photolysis of PI in the presence of vinyl acrylate: each **r** can form four secondary radicals: two “head-to-tail” and two “head-to head”.

Photolysis of **TPO** in the presence of vinyl acrylate lead to the main adduct presented in Scheme 6 and Scheme 9 below. However, a weak signal, which is ascribed to an adduct to vinyl ether group, is also observed in TR ESR spectra. The ratio of the

intensities of two ESR signals is ca. 20:1. This ratio is in good agreement with the ratio of rate constant of addition  $k_{\text{add}}$  of phosphinoyl radicals to acrylate group and to vinyl ether group (in a model compound vinyl pivalate) as 17:1.<sup>5</sup> Experimental data demonstrate that polyacrylate is the main product of free-radical polymerization of vinyl acrylate.<sup>9</sup>

We did not observe any adducts of substituted benzoyl radical during the time of observation of phosphinoyl adducts. *Thus, we observed one main adduct and the second adduct (in the much lower concentration) instead of eight adducts.*

TR ESR allows not only identifying short-lived radicals, but also for insights into their conformation. Analysis of the ESR spectra of adducts of phosphinoyl radicals to acrylates reveals that these secondary radicals have two conformations:



**Scheme 9.** *Cis-trans* isomerization of acrylate adduct radicals.<sup>5</sup>

Hindered rotation along a single bond manifests itself as broadening of TR ESR spectra components.

The same conclusions on the primary and secondary radicals can be achieved by steady-state (SS) irradiation in the ESR cavity which we call it SS ESR. SS ESR has several advantages and disadvantages as compared to TR ESR. First, SS ESR allows for detection of all free radicals, not necessarily only those in non-Boltzmann population (polarized). Second, SS ESR has high sensitivity towards paramagnetic species in low concentration because of the field modulation. SS ESR spectra are presented in the well-known form as the first derivative of the signal. On the other hand, it is not easy to detect highly reactive free radicals by SS ESR due to their low SS concentration.

## Termination

Termination of free radical polymerization is a reaction between two macroradicals ( $R_n^\cdot$ ):

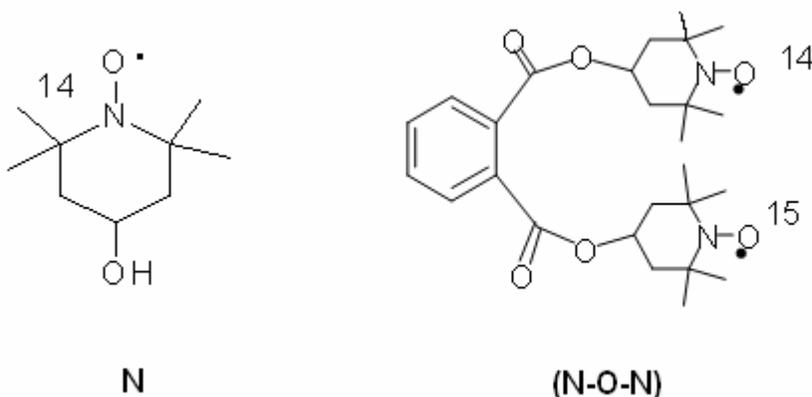


or between  $R_n^\cdot$  and any other reagent **X** leading to disappearance of reactive radicals:



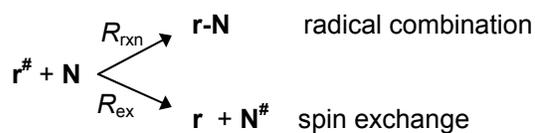
Using TR ESR, we studied a model reaction between free radicals of PIs and stable nitroxyl radicals of TEMPO family (**N**) and nitroxyl biradicals (**N-O-N**), with

radical termini being in proximity to each other, cf. Scheme 10:



**Scheme 10.** Chemical structure of 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPOL, **N**) and biradical (**N-O-N**). We used both symmetric (**N-O-N**) with <sup>14</sup>N isotopes and asymmetric (**N-O-N**) with <sup>14</sup>N and <sup>15</sup>N isotopes like the one presented in this Scheme.

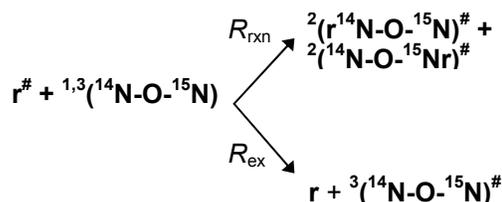
Both stable nitroxyls and nitroxyl biradicals are known as inhibitors of free-radical polymerization: they intercept reactive free radicals. Scheme 11 below presents processes occurring upon encounter of **r<sup>#</sup>** and **N**:



**Scheme 11.** Competition between chemical reaction (cross section  $R_{\text{rxn}}$ ) and spin exchange (cross section  $R_{\text{ex}}$ ) of reactive polarized radical **r<sup>#</sup>** and a nitroxyl radical **N**.

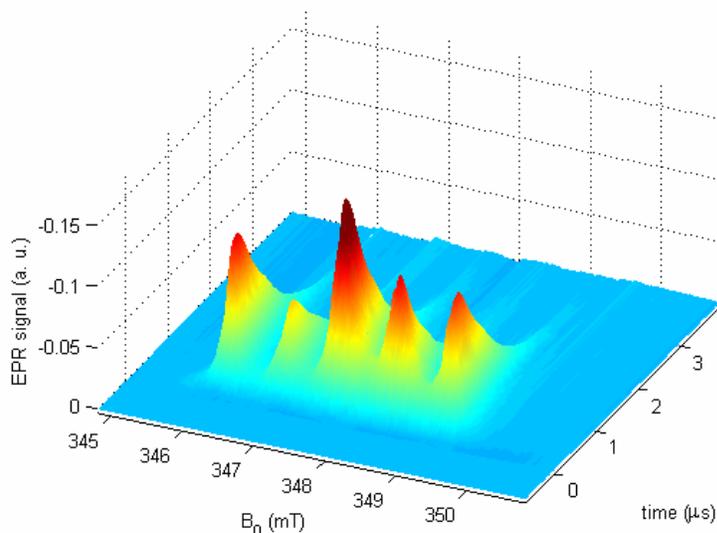
The diamagnetic molecular combination product **r-N** is evidently invisible by ESR, but we can state that radical **r<sup>#</sup>** was in proximity of stable nitroxyl **N** because TR ESR spectrum of **N<sup>#</sup>** was observed. Polarization transfer from one radical to another occurs by spin exchange.<sup>3</sup> It is believed that spin exchange does not require physical contact of the reagents, and it can occur at the distance of one or several molecular diameters between radicals. Discussion of spin exchange and its competition with chemical is presented elsewhere.<sup>10</sup>

In the case of a reaction of **r<sup>#</sup>** with (**N-O-N**) two polarization transfers, the following occur: 1 - by spin exchange with an appearance of (**N-O-N**)<sup>#</sup> and 2 - by addition of **r<sup>#</sup>** to (**N-O-N**) with formation of polarized monoradical:



**Scheme 5.** Competition between chemical reaction (cross section  $R_{\text{rxn}}$ ) and spin exchange (cross section  $R_{\text{ex}}$ ) of reactive polarized radical  $\mathbf{r}^\#$  and asymmetric nitroxyl biradical ( $^{14}\text{N-O-}^{15}\text{N}$ ).

In the case of symmetric ( $^{14}\text{N-O-}^{14}\text{N}$ ) one observes only one polarized monoradical (substituted TEMPO) and ( $^{14}\text{N-O-}^{14}\text{N}$ )<sup>#</sup>. A relatively simple TR ESR 2D spectrum that was obtained during photolysis of **IRG** in the presence of ( $^{14}\text{N-O-}^{14}\text{N}$ ) is demonstrated below:



**Figure 4.** 2D-TR-EPR spectrum produced by photolysis of **IRG** in the presence of ( $^{14}\text{N-O-}^{14}\text{N}$ ) in acetonitrile.<sup>10</sup>

## Conclusions

TR ESR allows one to identify structure and even configuration of free radicals, and helps in the understanding of their reactivity. Polarized and non-polarized radicals have the same reactivity because magnetic energy is negligible compared to thermal energy ( $kT$ ). Studying reactions in the magnetic field of X-band ESR spectrometer ( $\sim 0.3$  T) does not affect the reactivity of radicals towards multiple bonds of molecules. External moderate magnetic field can slightly decrease the rate constant of bimolecular self- or cross-recombination of free radicals.<sup>11</sup> Polarization of radicals is considered a non-invasive labeling of radicals, which allows following for observation of their fast reactions.

In some exceptional cases one can detect not only secondary polarized radical  $\mathbf{r-M}^\#$ , but even tertiary radical  $\mathbf{r-M-M}^\#$ .<sup>13</sup>

Unfortunately, TR ESR is impractical in determining rates of disappearance of radicals due to complex interplay of chemical reaction and paramagnetic relaxation.<sup>12</sup> Radical kinetics can be studied by laser flash photolysis with detection by absorption spectra. Light of the same pulsed laser can be directed into ESR cavity with a flow flat

cell or into optical cell of time-resolved spectrophotometer. Both cells may have the same solution.

During a microsecond time frame, which is the typical paramagnetic relaxation time of free radicals, polarized free radicals can participate in addition to multiple bonds, to dioxygen, in hydrogen (electron) transfer, in the addition to polyradicals, etc. Products of these reactions are polarized in most cases, and they demonstrate TR ESR signals. In rare cases TR ESR signals of not only secondary but a tertiary radical can be observed.

The same conclusions on the primary and secondary radicals can be achieved by SS ESR. TR ESR allows relatively simple observation of highly reactive transient free radicals. The method is especially convenient in the case of transient radicals with few magnetic nuclei, i.e., with a simple ESR spectrum.

## Acknowledgements

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