

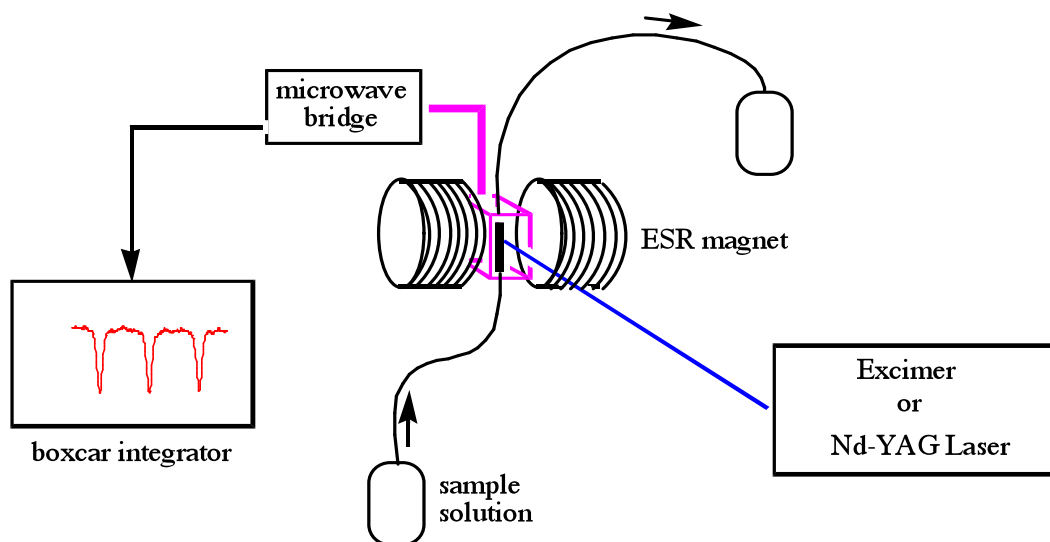
# Interaction of Photoexcited Photoinitiators with Nitroxyl Radicals

Igor V. Khudyakov

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

**Introduction.** Formulations which undergo photopolymerization have in most cases photoinitiators (PI) like Darocur, Irgacure, benzophenone, others. These formulations may have nitroxyl radicals, which are added for prevention of degradation of the cured coatings. Nitroxyls are formed during oxidation of HALS stabilizers also. Thus, there is a possibility of interaction of photoexcited PI with nitroxyl. This process was studied ns laser flash photolysis and by time-resolved (TR) ESR. The pattern of TR ESR spectra provides valuable information on the interaction of one or another excited state with a stable radical.

**Devices and Chemicals.** We used TR ESR of X-band, cf. Scheme 1:

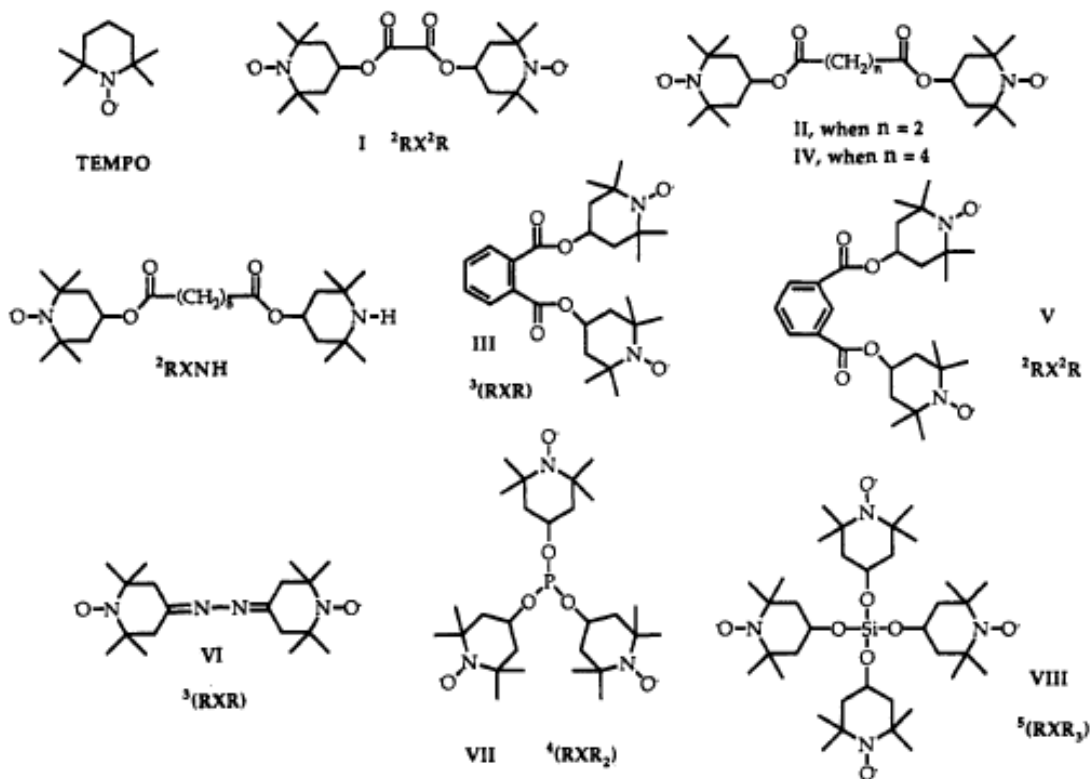


*Scheme 1*

The screen of boxcar integrator in the Scheme 1 demonstrates a transient emissive ESR signal of nitroxyl radical (three components or three lines). Minor modification of the device allows returning it to a standard ESR spectrometer.

One will get the known ESR spectrum of the same nitroxyl in its usual form – as the first derivative.

We used common nitroxyls TEMPO and others and polynitroxyls of the following structures:



Scheme 2

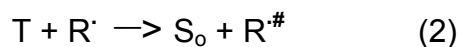
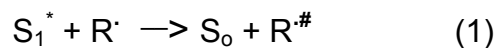
In this work we report results obtained with PI diphenyl(2,4,6 trimethylbenzoyl)phosphine oxide or MAPO, or Lucerin TPO, benzil dimethyl monoketal or Irgacure 651 and benzophenone (BP).

Laser flash photolysis experiments and TR ESR experiments were performed at room temperature in non-viscous solvents.

## Results and Discussion.

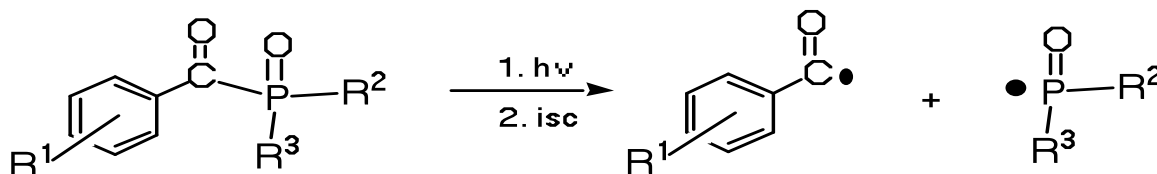
**1. Quenching.** Electronically excited states of organic molecules are usually effectively quenched by stable free radicals. Often quenching is *not* accompanied

by a net photochemical reaction (eqs 1, 2) and represents the interaction of an electronically excited state and a paramagnetic species, a radical:



Sign # stands here and below for polarization of a radical in the magnetic field, which means non-Boltzmann population of Zeeman levels of a radical in magnetic field, cf. refs 1-3. (Seminal contributions of research groups from several countries into TR ESR and CIDEP studies are cited in our publications.<sup>1-8</sup>)

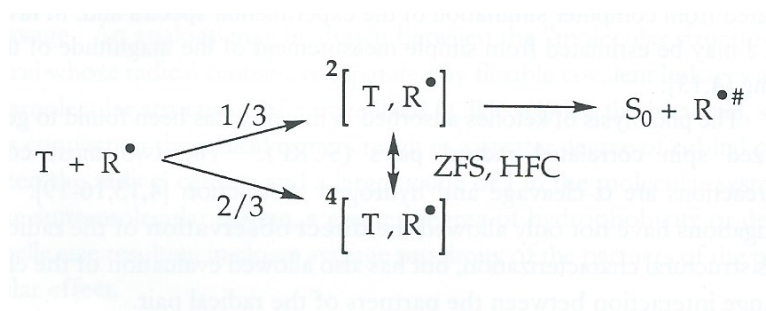
PI usually initiates polymerization being in the excited triplet state T and reaction 2 is important. Fortunately, most of Irgacures and Darocur *dissociate very fast into reactive free radicals*:



### Scheme 3

Life-time  $\tau$  of MAPO triplet is very short, namely  $\sim 100$  ps,  $\tau$  of BAPO triplet is  $\sim 300$  ps. That means that *nitroxyl radicals existing in a relatively low concentration in the coating (as well as dissolved in the coating air dioxygen) should not affect photodissociation of Irgacures and Darocur.*

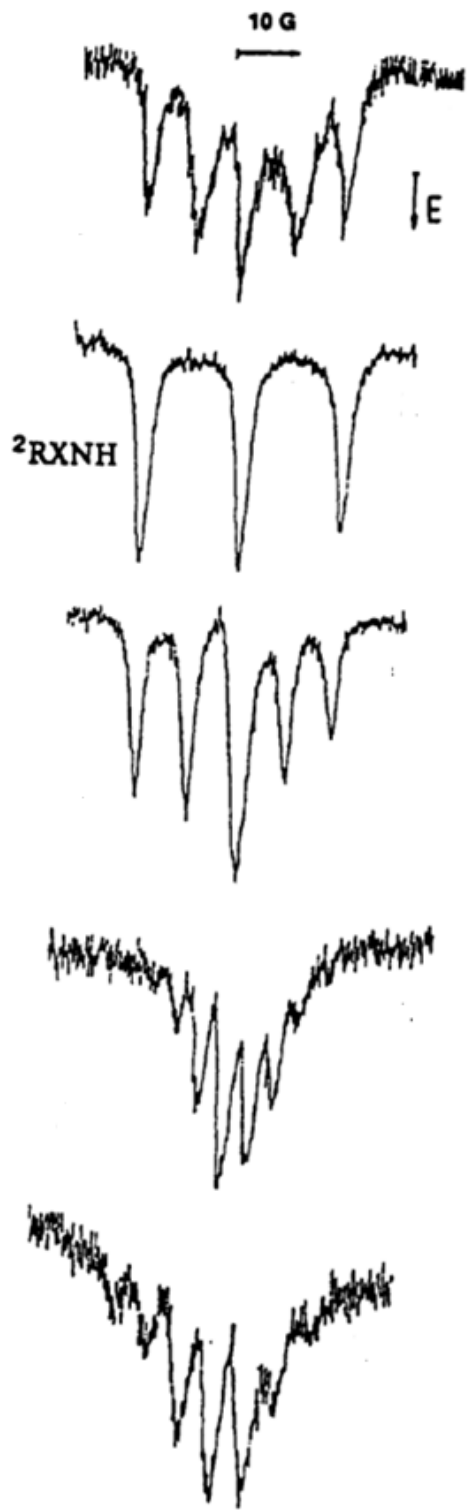
BP, a Type II PI, participates in a hydrogen abstraction (or in electron transfer with a subsequent proton transfer).<sup>9</sup> At the same time triplet BP (T) can interact with nitroxyl radical  $R^\cdot$  by reactions presented in the Scheme 4 below:



*Scheme 4*

Triplet and a radical form two different pairs, one is in a doublet and another is in a quartet electronic state. As a result of this interaction, nitroxyl R' becomes polarized, cf. for details refs 1-7. It is possible to conclude occurrence of reaction 2 not only by the fact of disappearance of T but by the observation of polarized R<sup>#</sup> as well. *TR ESR spectra of nitroxyl, which interacted with T molecules of PI, always appear as emission spectra*, cf. Figure 1 below.

>N-O' fragments of polynitroxyls which are located spatially close, interact with each other, and demonstrate not three components in the ESR spectra but more components. In particular, binitroxyl in the case of a relatively strong magnetic interaction of >N-O' fragments, demonstrates five components and most of the binitroxyl is in the triplet state <sup>3</sup>(RXR). (Here and below R stands for a nitroxyl fragment.) It is a case of so-called *strong exchange*, cf. below. Binitroxyl, which has >N-O' fragments spatially separated, is a case of *weak exchange*. ESR spectrum of the latter binitroxyl has three components; >N-O' do not interact with each other.

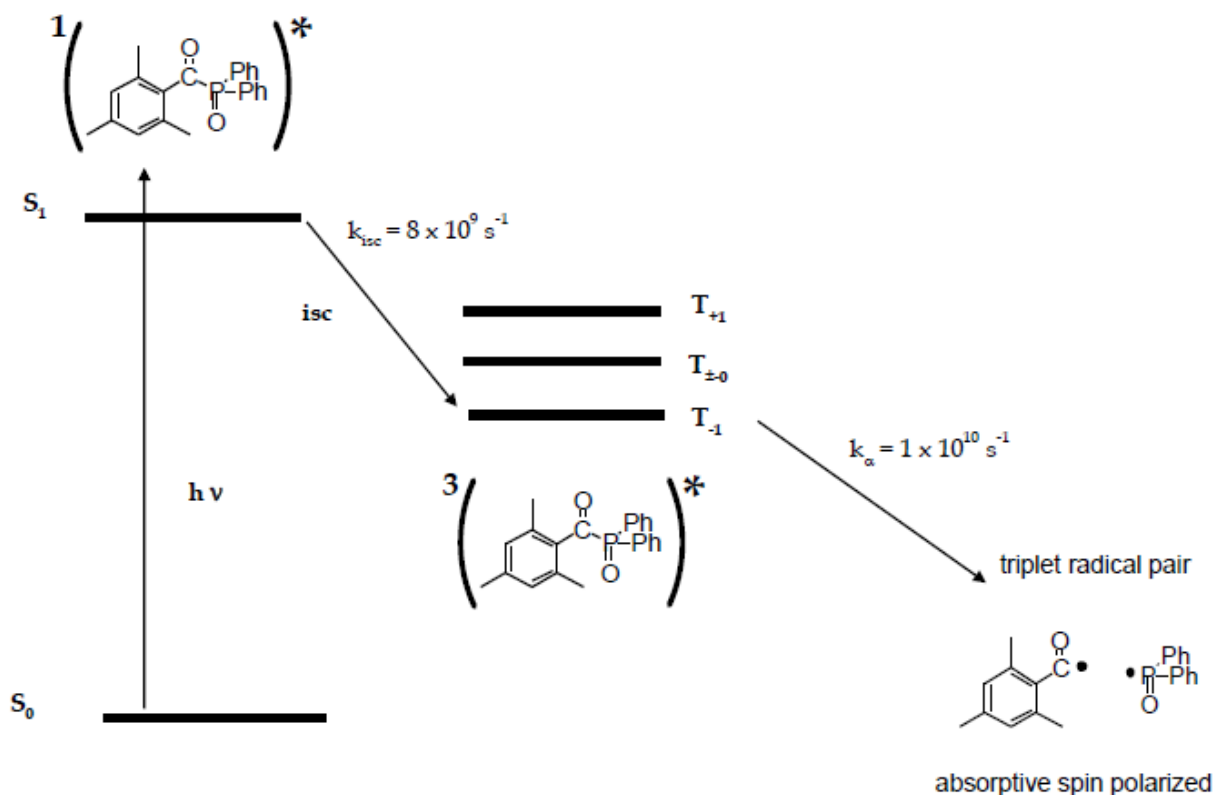


**Figure 1.** TR ESR spectra of several (poly)nitroxyls (cf. Scheme 2) obtained under laser photoexcitation of BP in the presence of corresponding (poly)nitroxyls. Spectra are taken at 300-600 ns after a laser flash.

Contrary to the triplet molecules case, *nitroxyls, which interact with singlet excited molecules (eq 1), demonstrate absorptive TR ESR spectra.* In our experience, singlet dioxygen  $^1\text{O}_2$  produced by photolysis of endoperoxide, is quenched by nitroxyl, and TR ESR spectrum of nitroxyl appears *in absorption*.<sup>1</sup>

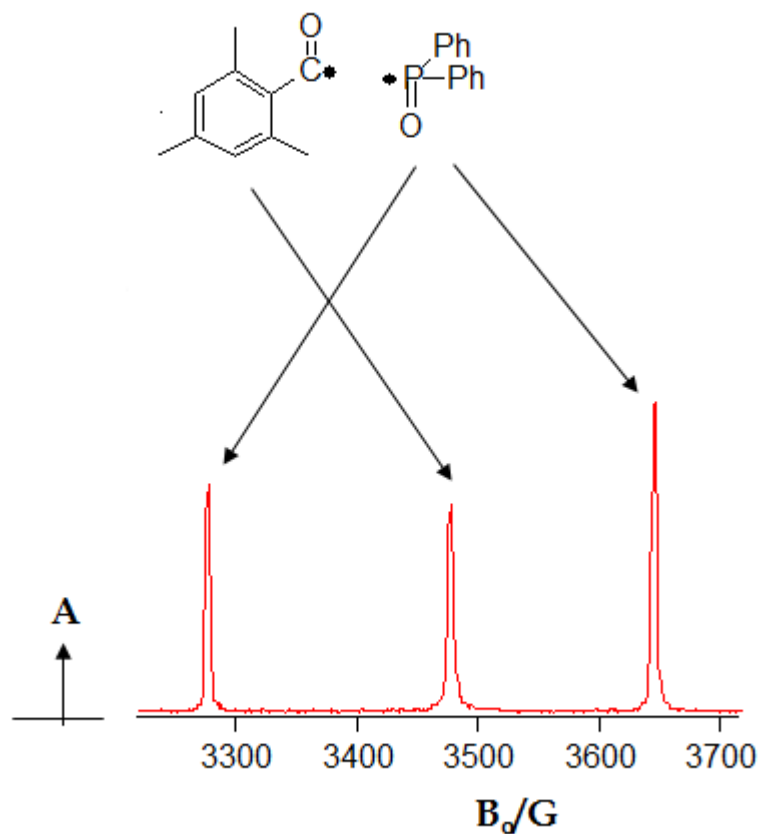
We omit discussion of time profile of nitroxyl TR ESR spectra and a complex case of strong dependence of intensities of components upon hyperfine coupling (HFC) constants of nitroxyl.

2. **Chemical reaction.** Free radicals of Type I PI manifest polarization in their TR ESR spectra. Scheme 5 below is a simplified presentation of origination of such polarization by a triplet mechanism:



Scheme 5

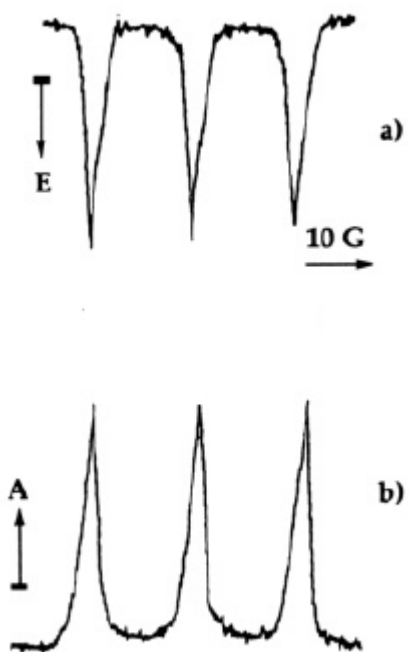
Scheme 5 presents a case of MAPO as an example. Well-documented spectra of two spin polarized radicals  $r^\#$  of MAPO are presented on the Figure 2:



**Figure 2.** TR ESR spectra of free radicals, which are primary products of the photolysis of MAPO. Spectra are taken at 50-150 ns after a laser flash.

Polarized radicals of PI are designated as  $r^\#$  in the present work. One can see from Figure 2, that  $r^\#$  of MAPO are in absorption.  $r^\#$ , observed under photolysis of Irgacure 651, are in emission.

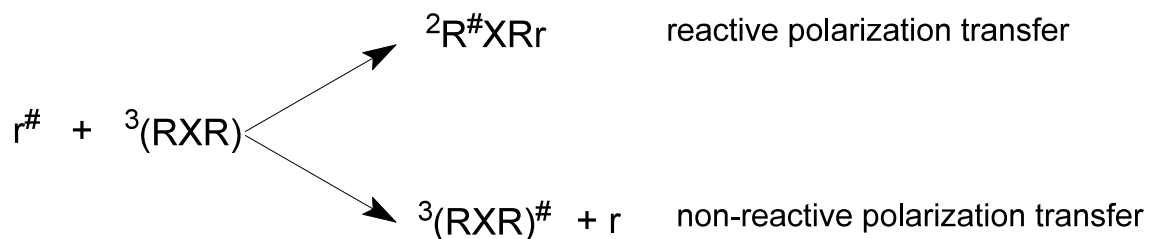
Photolysis of MAPO or Irgacure 651 in the presence of TEMPO (Scheme 2) leads to the following TR ESR spectra of TEMPO:



**Figure 3.** TR ESR spectrum obtained under photolysis of solutions of polarization donors (a) Irgacure 651 and (b) MAPO. Spectra are taken at 300-800 ns after a laser flash.

Figure 3 demonstrates that polarization of initial  $r^\#$  is transferred to TEMPO.

More interesting is the case of interaction of  $r^\#$  with binitroxyl in a strong exchange  $^3(\text{RXR})$  (cf. above). Two processes take place during interaction of  $r^\#$  with polynitroxyl in a strong exchange:

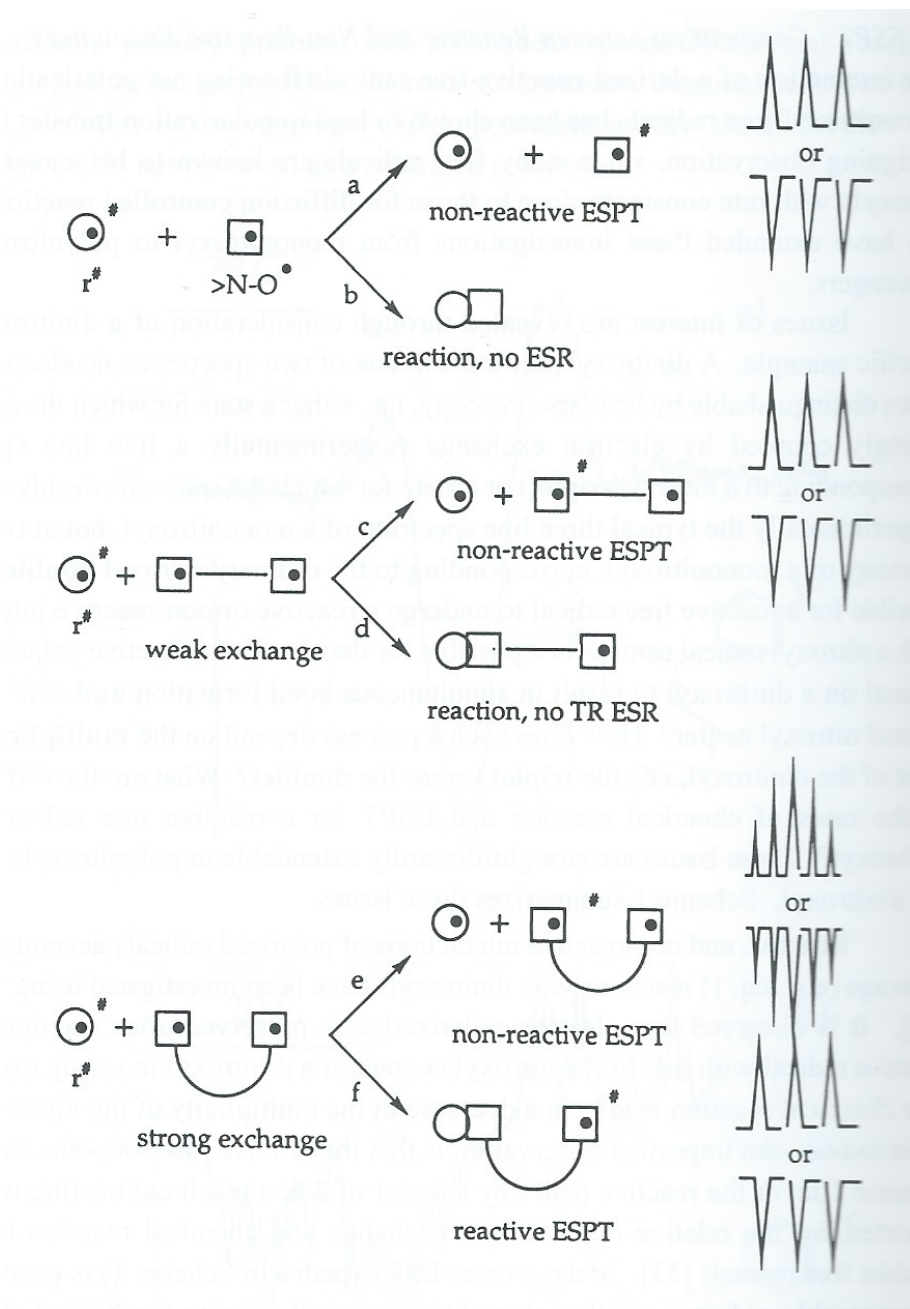


*Scheme 6*



They are a “*physical*” process of electron spin polarization transfer (ESPT) and ESPT in the fast *chemical* reaction.

In summary, Scheme 7 below is a pictorial demonstration of TR ESR spectra observed under interaction of absorptively or emissively polarized  $r^\#$  with mono- and binitroxyls in a strong and in a weak exchange:



Scheme 7

**Conclusions.** It is possible to study kinetics of elementary reactions proceeding during photopolymerization (UV-cure) of neat vinyl monomer up till conversion of 5-10%.<sup>8</sup> The system may be approximately considered as a Newtonian liquid, and one can get more or less reliable rate constants of elementary reactions, identify transient radicals, and quantitatively estimate efficiency of the used PI.

High rates of photodissociation of Type I common PI do not depend upon addition of nitroxyls. Quenching of triplet BP by (poly)nitroxyl leads to emissive TR ESR spectrum of the latter.

Free radicals of PI  $r^\#$  are highly reactive towards mono and polynitroxyls.  $r^\#$  demonstrate emissive or absorptive polarization. That polarization is transferred to (poly)nitroxyl radical by ESPT: non-reactive polarization transfer and in the course of concurrent chemical addition. Polarization causes radicals to be “labeled” but does not affect their chemical reactivity in chemical reactions, because the magnetic energy is negligible compared with the thermal energy  $k_B T$ . Polarization transfer is an excellent method for following the pathways of photoinduced free-radical chemical reactions or “physical” interaction of radicals with other radicals or excited states.

ns Laser flash photolysis with optical and ESR detection provides a powerful arsenal to investigate radical species produced in the photoinitiation of radical polymerization.

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