

Magnetic and spin effects in the photoinitiation of polymerization

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Abstract—Application of a moderate external magnetic field increases the efficiency of triplet photoinitiators of polymerization. The reasons for this observation are briefly outlined. Such well-documented magnetic and spin effects as the magnetic isotope effect (MIE) and chemically induced dynamic nuclear and electron polarization (CIDNP and CIDEP) have been observed under the photolysis of photoinitiators. CIDEP results are emphasized. The study of CIDEP under the photolysis of initiators allows the detection and identification of free radicals of initiators and the spin multiplicity of the reacting photoinitiator (triplet or singlet). The transfer of the spin polarization of the initiator free radical to monomers is a promising technique for following radical reaction pathways. The results of a CIDEP study of the sensitized decomposition of phosphine oxide photoinitiators are presented.

Keywords: Polymerization; radical pairs; magnetic field; isotope effect.

1. INTRODUCTION

Free radical photopolymerization is accompanied by the formation of transients with a non-zero spin angular momentum: free radicals, radical pairs, and the triplet states of photoinitiators. A stable molecule in a triplet state, such as molecular oxygen, plays an important role in polymerization. One can expect the manifestation of a magnetic and spin effect in free-radical photopolymerization. The magnetic and spin effect has been known in physical chemistry and photochemistry for three decades [1–5]. A number of mechanisms for the magnetic field effects (MFEs) in chemical reactions have been established, well documented, and have received a proper theoretical analysis. However, applications of MFEs to photopolymerization are rather limited and deserve further exploration.

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The primary event of the photoinitiation of free-radical polymerization is the formation of a radical pair R^* , R^* being the result of a bond cleavage, or hydrogen atom or electron abstraction by a photoinitiator. Radical pairs (RPs) are important intermediates and their self-reactivity (cage effect) influences the efficiency of polymerization. The outcome of a photochemical reaction essentially depends on the spin evolution of RP intermediates. The reactivity of a RP is sensitive to the application of an external moderate magnetic field. This report is a brief review of the experimental manifestation of magnetic and spin effects in the reactions of photoinitiators and in a photopolymerization. We have used experimental results obtained in our laboratories as an illustration. The role of alternating magnetic fields and microwaves on photoinduced and free radical reactions is beyond the scope of this paper.

2. MAGNETIC FIELD EFFECTS IN PHOTOPOLYMERIZATION

Fig. 1 demonstrates an idea of the MFE as the photodissociation of an initiator of polymerization in a triplet state. In most cases, triplet RPs formed under the photodissociation of an initiator in a triplet state cannot recombine. Thus, it is not surprising that most of the commercially available photoinitiators of polymerization dissociate exclusively in a triplet state. A certain fraction of RPs undergo inter-system crossing into the singlet state and recombine inside a cage. The application of a moderate external magnetic field ($B > A_{\text{eff}}$) decreases the efficiency of inter-system crossing. A_{eff} , the effective hyperfine coupling (HFC) constant of RP, for many pairs with HFC to protons is *ca.* 50 G. Thus, the application of a moderate magnetic field can increase the exit of radicals from a solvent cage, which increases the initiation rate of polymerization. This is the essence of the MFE occurring according to the HFC mechanism. The relative wideness of the arrows in Fig. 1 indicates the relative rates or efficiencies of the processes; the wider the arrow, the faster the process.

In practice, such S–T evolution occurs relatively slowly for RPs with a specified A_{eff} , and a reduction in the mobility of a RP is required for the manifestation of a MFE. A reduction in mobility can be achieved in different ways: by using inclusion a RP in a micelle; by an increase in solvent viscosity, etc. Free radical polymerization accompanied by a viscosity increase is a promising process for the manifestation of MFEs.

MFEs were observed for the first time in the emulsion polymerization of styrene photoinitiated by dibenzyl ketone (see Fig. 2) [6, 7].

Application of a moderate magnetic field of 50–1000 G significantly accelerated the polymerization and resulted in an increase of the molecular weight (MW) of polystyrene formed in the emulsion polymerization, due to the HFC mechanism of MFE [6, 7]. Experiments on the photopolymerization of acrylamide initiated by the dye Methylene Blue in a viscous water–glycerol solution and on the photopolymerization of *N,N,N,N*-dimethyldiallyl ammonium chloride in an aqueous

Singlet vs. Triplet Radical Pairs

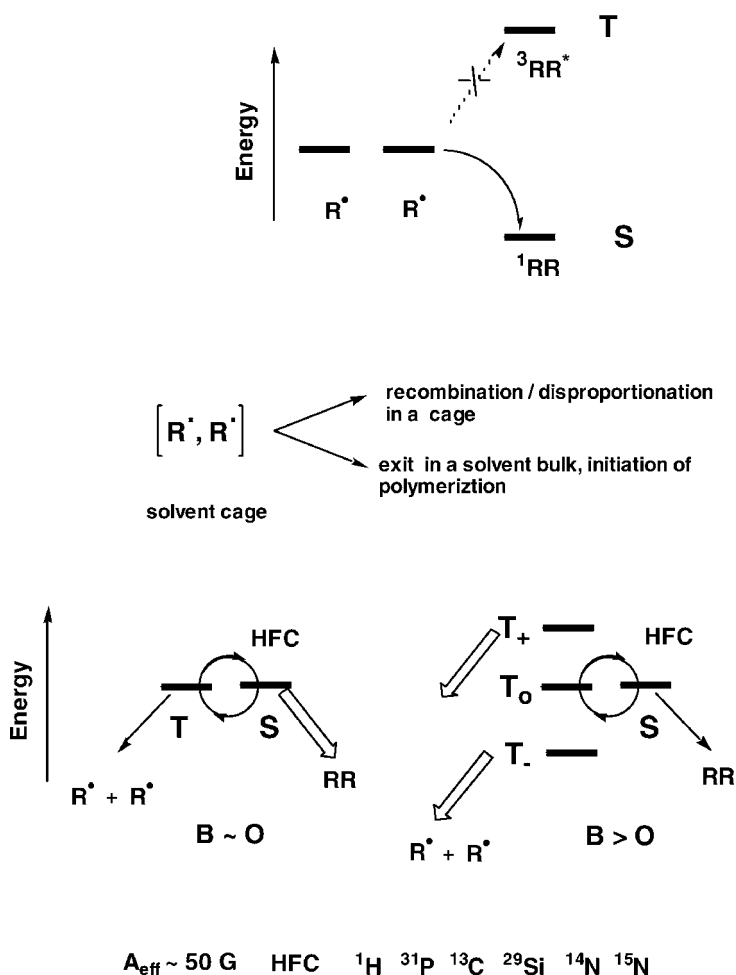


Figure 1. Schematic representation of the hyperfine coupling mechanism of a MFE.

solution initiated by uranyl salt resulted in acceleration of the polymerization and a reduction in the MW of the formed polymer [5, 8]. Fig. 3 demonstrates the MFE in the polymerization of acrylamide.

The magnitudes of the MFEs observed so far in homogeneous solutions have been rather small. Fig. 4 presents recent data on the polymerization of neat methyl methacrylate (MMA) and two other monomers initiated by 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1, known as Irgacure 907 of Ciba Additives.

Some data on MFEs in polymerization are compiled in review articles [9, 10].

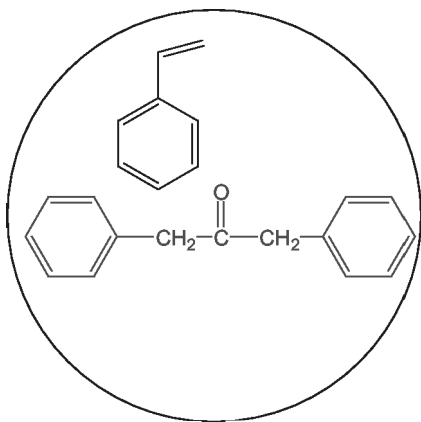


Figure 2. Diagram of a SDS micelle containing the photoinitiator dibenzyl ketone and styrene.

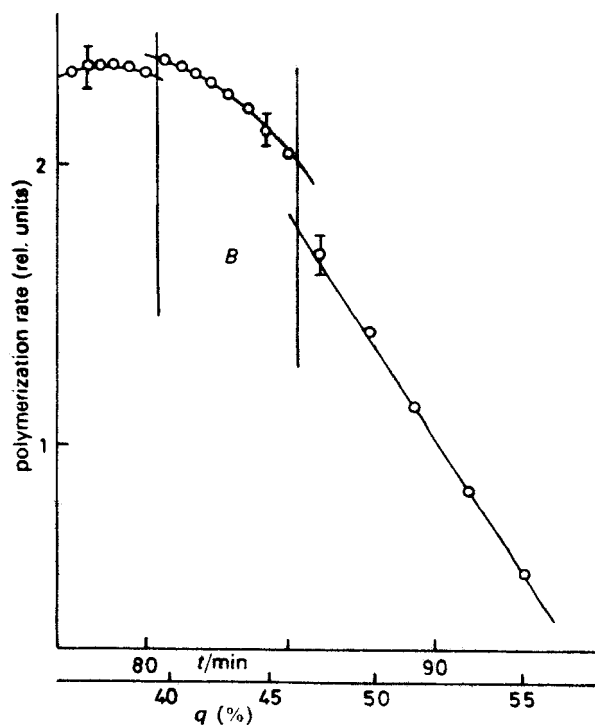


Figure 3. Time-dependent rate of the polymerization of acrylamide in air-saturated water–glycerol mixture containing Methylene Blue and triethanolamine. q stands for the conversion of a monomer. The period of application of a magnetic field of 1000 G is marked on the plot [8].

3. MAGNETIC ISOTOPE EFFECT UNDER THE PHOTOLYSIS OF INITIATORS

Magnetic isotope effect (MIE) separation of magnetic (with non-zero spin angular nuclear momentum) and non-magnetic isotopes has been observed under the

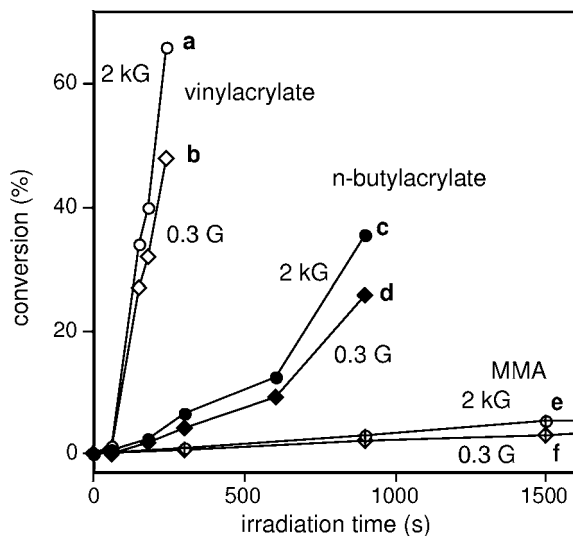
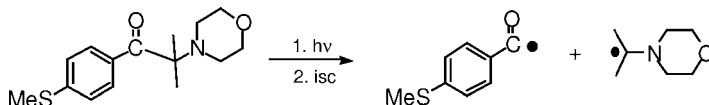


Figure 4. Photoinduced radical polymerization of vinylacrylate (3.2 M) (a, b), n-butylacrylate (4.7 M) (c, d), and MMA (6.2 M) (e, f) in an air-saturated methylene chloride solution (2 : 1, v/v) initiated by the irradiation of Irgacure 907 (cw lamp λ 366 nm; ~ 62 mW/cm²) in the presence (a, c, e) and absence (b, d, f) of an external magnetic field (2 kG and 0.3 G, respectively; N. Arsu and S. Jokusch, unpublished results).

photolysis of such photoinitiators as dibenzyl ketone and uranyl salts [1–5]. Figure 5 presents a scheme of the MIE. Photolysis of an initiator A occurs via a triplet state. A has a natural or a special level of a magnetic isotope; such A with magnetic isotopes is denoted as A[#]. Photolysis of A[#] occurs with the formation of a radical pair which has an additional HFC on a magnetic isotope, compared to the photolysis of A. Such triplet RPs with a magnetic isotope undergo faster intersystem crossing into singlet RPs with the formation of a cage product enriched with a magnetic isotope. Prolonged photolysis of A/A[#] in the earth's magnetic field or in a moderate external magnetic field results in a measurable separation of isotopes.

A detailed analysis of the MIE can be found in Refs. [1] and [4].

4. CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION (CIDNP) UNDER THE PHOTOLYSIS OF INITIATORS

Photolysis and thermolysis of the initiators of polymerization in the cavity of an NMR spectrometer is accompanied by CIDNP, i.e. by the formation of products with a non-Boltzmann population of nuclear Zeeman levels. CIDNP manifests itself

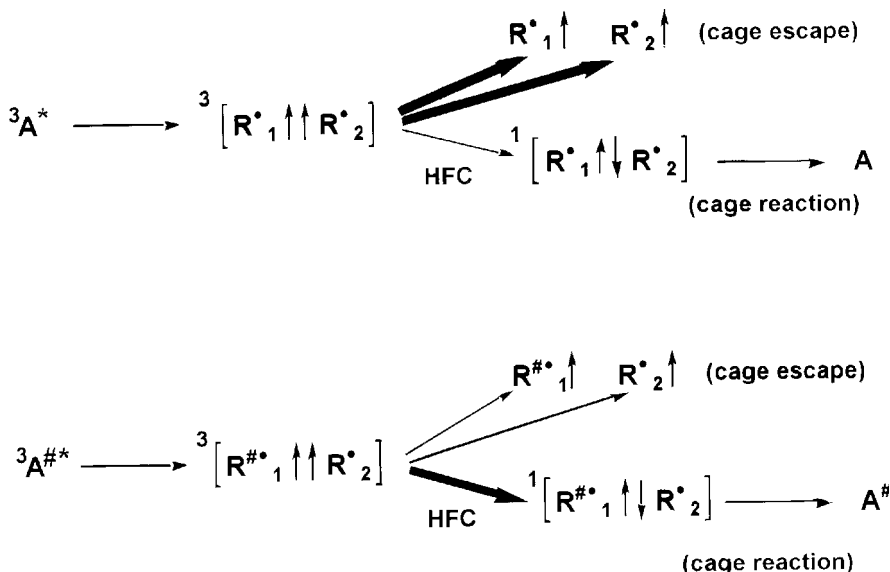


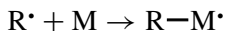
Figure 5. Scheme explaining the action of MIE (see text).

in the enhanced absorption or emission of certain components in the NMR spectra of the products of free-radical reactions. Study of CIDNP allows an understanding of the origin of the diamagnetic products of free radical reactions. A multitude of CIDNP experiments have been performed with ${}^1\text{H-NMR}$, ${}^{31}\text{P-CIDNP}$ under the photolysis of phosphine oxide photoinitiators. ${}^1\text{H-CIDNP}$ is important for a detailed study of these very efficient photoinitiators. ${}^1\text{H-CIDNP}$ was studied under the photolysis of uranyl salts and uranyl complexes in Refs. [11–13] (see Fig. 6).

5. CHEMICALLY INDUCED DYNAMIC ELECTRON POLARIZATION (CIDEP) UNDER THE PHOTOINITIATION OF POLYMERIZATION

Flash photolysis of the initiators of polymerization in the cavity of an ESR spectrometer is often accompanied by CIDEP, i.e. by the formation of radicals with a non-Boltzmann population of electron Zeeman levels. CIDEP manifests itself in the enhanced absorption or emission of all or certain components in the ESR spectra of photogenerated free-radicals. The main mechanisms leading to CIDEP in photoinduced reactions are well established [14, 15].

Study of the CIDEP pattern of time-resolved (TR) ESP spectra allows the establishment of solid conclusions on the spin multiplicity of molecular precursors of polarized free radicals (singlet or triplet excited molecules) and the tracking of fast reactions of polarized radicals leading to secondary radicals. An important reaction of this type is the addition of a free radical of a photoinitiator (R^{\bullet}) to a monomer (M):



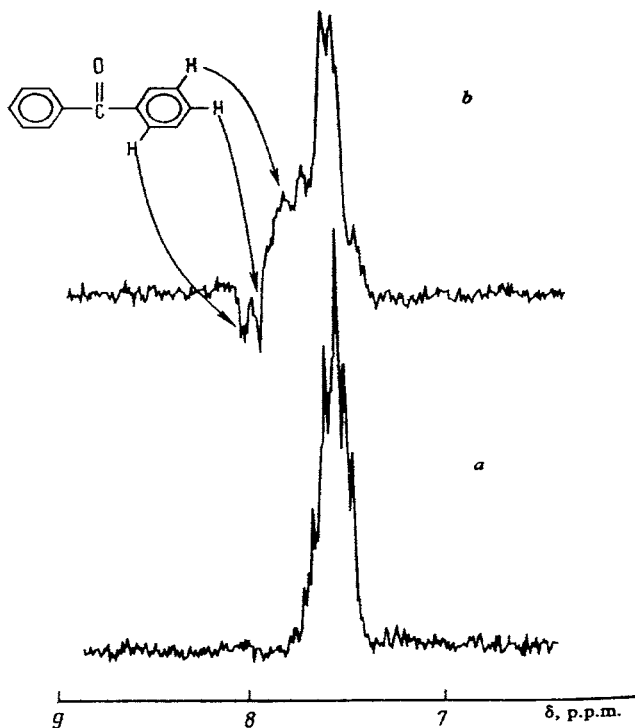
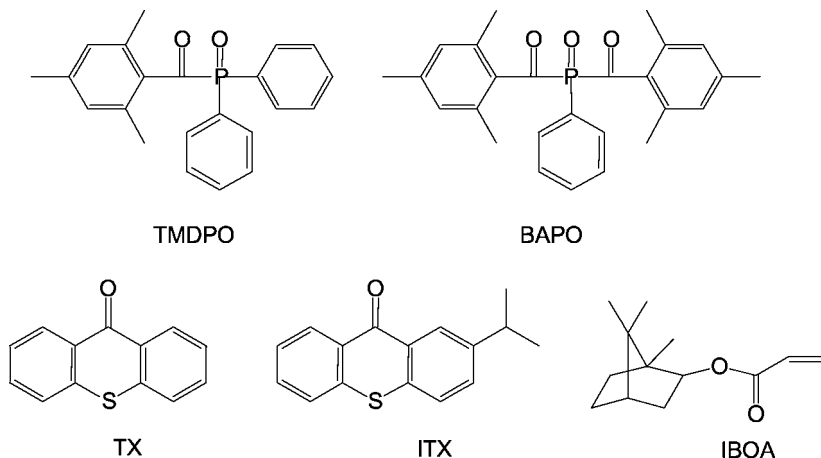


Figure 6. Top: $^1\text{H-NMR}$ of 2,6-di-*t*-butylphenol and uranyl nitrate in methanol- d_4 (a) before and (b) during irradiation. Bottom: $^1\text{H-NMR}$ of acidified methanol- d_4 solution of benzylic acid and uranyl nitrate (a) before and (b) during irradiation. In these experiments, uranyl nitrate absorbed light [13].

As an example, we will consider direct and sensitized photoinitiation with phosphine oxides in the polymerization of isobornyl acrylate [16]. Chemical structures and abbreviations of the names of the compounds studied are presented below:



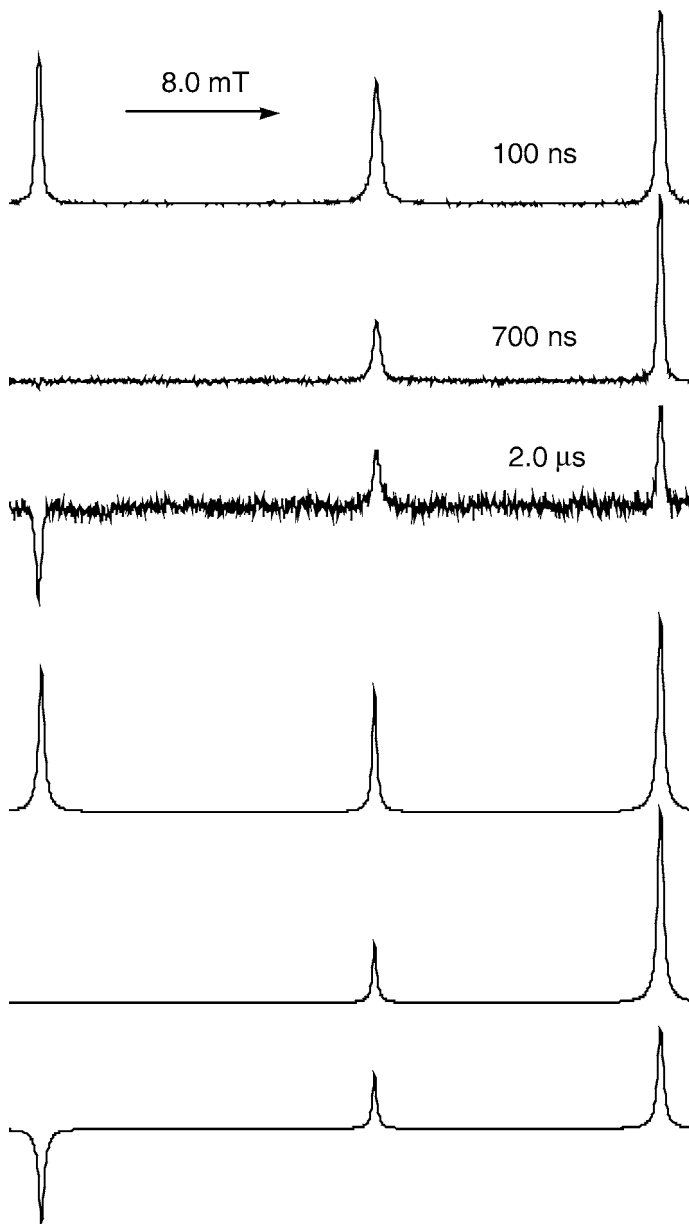


Figure 7. TR ESR spectra of TMDPO in ethyl acetate taken at different times and computer-simulated spectra. A solution of TMDPO was subjected to pulse laser excitation [16].

The direct photolysis of phosphine oxides results in a well-documented initial strong absorptive (A) pattern of ESR spectra (see Fig. 7). TX- sensitized or ITX photolysis of phosphine oxides evidently leads to the same radicals, but the initial polarization pattern is quite different, namely an emission/absorption (E/A) pattern

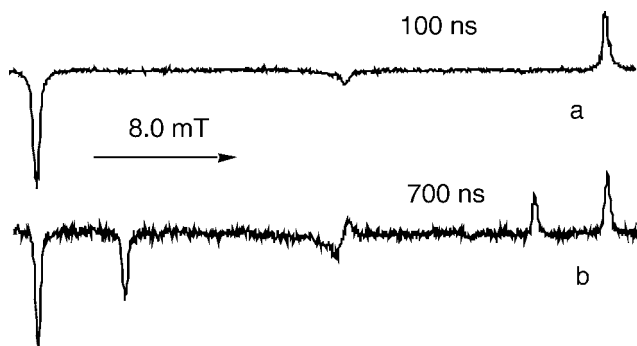


Figure 8. TR ESR spectra in ethyl acetate of: (a) TMDPO in the presence of TX; (b) a mixture of TMDPO and BAPO in the presence of ITX. Solutions were subjected to pulse laser excitation, light was absorbed mainly by triplet sensitizers [16].

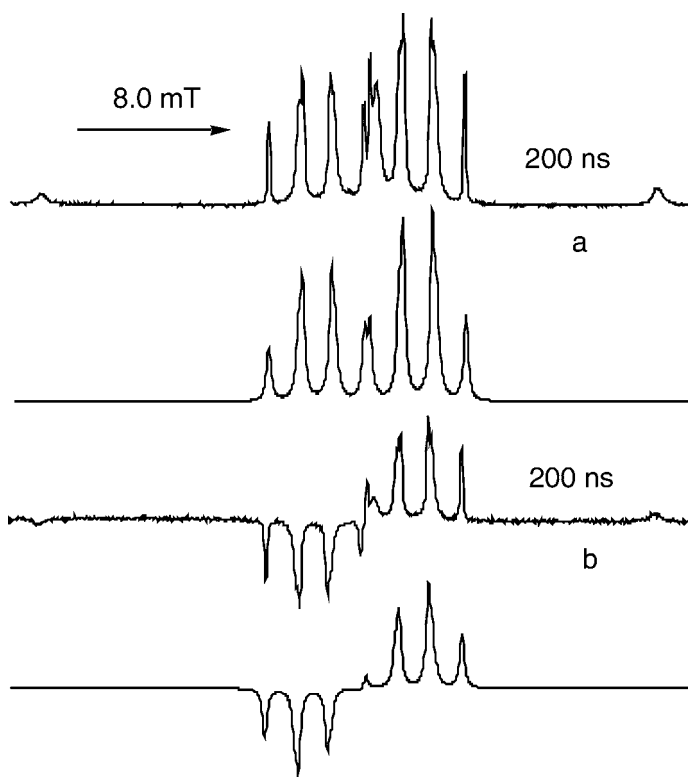
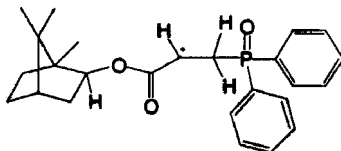


Figure 9. TR EPR spectra in ethyl acetate of: (a) TMDPO in the presence of IBOA; (b) TMDPO in the presence of TX and IBOA. Computer-simulated spectra are also shown below the experimental spectra [16]. Solutions were subjected to pulse laser excitation. See text for discussion.

(see Fig. 8). Thus, observation of the pattern of TR ESR spectra allows the determination of the reaction pathway leading to the same radicals. In our case, it is direct vs. sensitized photolysis.

TR ESR spectra obtained after the addition of IBOA to solutions under investigation are presented in Fig. 9. The observed spectra consist mainly of polarized signals of spin adducts of phosphinoyl radical and acrylate:



The spectra presented in Figs 7–9 demonstrate that the polarization pattern is preserved during the fast addition of radicals to a monomer. Absorptive (A) polarization observed under the direct photolysis of photoinitiators (Fig. 7) results in an A pattern of the spectrum of a spin adduct (Fig. 9a) and the E/A pattern observed under sensitized photolysis (Fig. 8) results in an E/A pattern of the spectrum of a spin adduct (Fig. 9b). Thus, TR ESR study allows the establishment of not only the origin of free radicals, but also their reactions.

In some special cases, it is possible to trace the polarized tertiary radicals formed in a reaction:



A tertiary polarized radical was observed in particular under the photolysis of TMPDO in the presence of *t*-butyl acrylate [17].

6. CONCLUDING REMARKS

Magnetic and spin effects in photoinduced chemical reactions have been extensively studied experimentally and theoretically. Application of a magnetic field affects the rates and molecular weights of polymers formed in free radical polymerization. The use of a magnetic field in free radical polymerization has not yet found a practical application, to the best of our knowledge. We can speculate that a magnetic field can be used in cases where MFEs are significant, or when a non-intrusive influence on the rate of polymerization is required, or when there is a need to increase the efficiency of a costly photoinitiator.

TR ESR study of photoinitiators and their reactions is very promising for an understanding of chain initiation in free radical polymerization. The CIDEP pattern allows the origin of free radicals and their fast subsequent reactions to be traced. The most important such reaction is addition to a monomer.

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