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Radical Polymerization

Decisive Reaction Steps at Initial Stages of Photoinitiated Radical Polymerizations**

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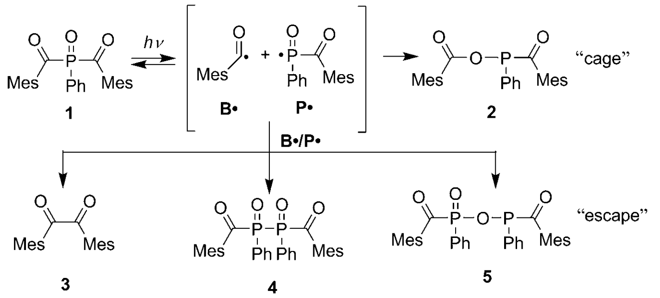
Radical polymerization has been the focus of interest in terms of synthetic, technological, and mechanistic aspects.[1–3] Many photoinitiating systems have been investigated, in which magnetic resonance methodologies were used as an exceedingly convenient tool to analyze the primary products.[4–6] More recent developments in radical polymerization involve "living procedures",[7–9] which result in a rather uniform molecular-weight distribution. Reversible addition/elimination steps are decisive for living radical polymerization procedures.[9–13] Reversible steps in "classical" radical polymerizations have been established in the case of depolymerizations (decompositions)[14–17] and during chain growth (also characterized by the ceiling temperature).[4,18–23] Another important feature of photoinitiated radical polymerizations is the formation of benzaldehyde derivatives even at early stages of the polymerization.[24]

Here we address mechanistic aspects of the reversibility and formation of aldehydes by using ^{1}H CIDNP (chemically induced dynamic nuclear polarization) spectroscopy[25] to follow the very early steps of the radical polymerization. CIDNP is a particularly suitable tool for these investigations since the subsequent products formed from chemical reactions involving radical pairs are observed exclusively.

Here, bisacylphosphine oxide **1** serves as an ideal model compound because it is a well investigated[3,6,26] and frequently utilized[3] commercially available photoinitiator. It has been shown that photolysis of **1** leads to benzoyl radical **B**$^{\cdot}$ and phosphinoyl radical **P**$^{\cdot}$ (Scheme 1).[27] In the absence of a quencher, **B**$^{\cdot}$ and **P**$^{\cdot}$ either recombine to yield parent **1** or form products **2**–**5** through either "cage" or "escape" reactions.[27] In the presence of, for example, acrylates, radicals **B**$^{\cdot}$ and **P**$^{\cdot}$ initiate polymerization, and the rate constants for the addition of **B**$^{\cdot}$- and **P**$^{\cdot}$-type radicals to double bonds were determined by time-resolved optical, IR, and EPR spectroscopy.[6,26,28]



Scheme 1. Radical products (**B**$^{\cdot}$ and **P**$^{\cdot}$) formed after photocleavage of bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide **1** and the "cage" (**1** and **2**) and "escape" products (**3**–**5**) formed by recombination. Mes = mesityl = 2,4,6-trimethylphenyl.

The first question is whether the first addition to an acrylate and the following growth of the polymer chain is the only subsequent reaction of the initial radical pair **B**$^{\cdot}$/**P**$^{\cdot}$. To begin with, a mixture of **1** and the sterically congested acrylate ***t*-BAM** (3,3-dimethyl-2-methylenebutanoate, molar ratio **1**/***t*-BAM** = 1:1–1:20) or butyl acrylate (**BA**, molar ratio **1**/**BA** = 1:1–1:20) was irradiated in [D$_6$]benzene and [D$_3$]acetonitrile. The ^{1}H CIDNP technique afforded NMR spectra of products formed exclusively from radical pairs on a short time scale (ns–μs).[25,29] Figure 1 compares the ^{1}H NMR spectrum of the parent reaction mixture of **1** and ***t*-BAM** (top) with the corresponding ^{1}H CIDNP spectrum obtained after photolysis with a Hg-Xe lamp (300 ms). Bearing in mind that only signals of products formed via paramagnetic intermediates are visible

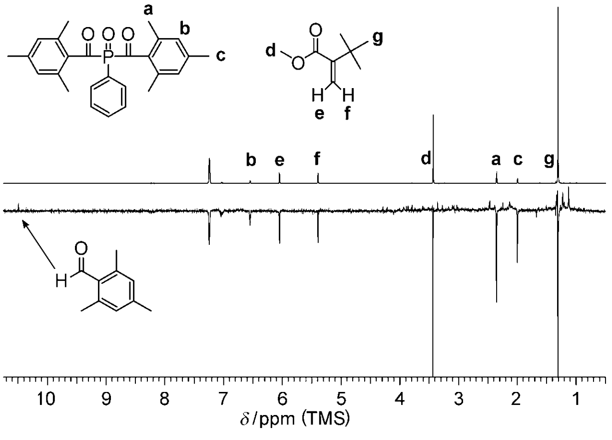


Figure 1. Top: ^{1}H NMR spectrum of **1**/***t*-BAM** (1:10) in C$_6$D$_6$. Bottom: The corresponding ^{1}H CIDNP spectrum recorded immediately after irradiation.

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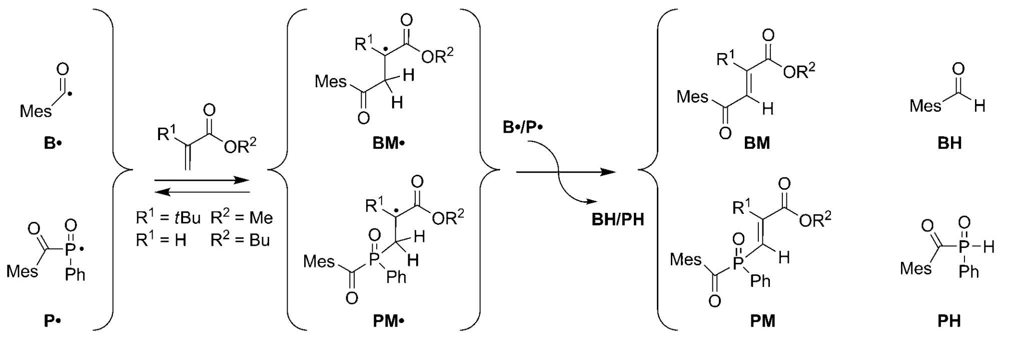
in the CIDNP experiment, it is, at first sight, surprising that the signals of ***t*-BAM** ($\delta = 5.31$ and 5.97 ppm) appear as being "polarized" in the ^{1}H CIDNP spectrum. This observation reveals that ***t*-BAM** must be regenerated through a pathway involving a radical pair, which can be rationalized by assuming that the initial addition of ***t*-BAM** to **B**$^\bullet$ and **P**$^\bullet$ is reversible (Scheme 2). The reversibility may be due to steric congestion of the *tert*-butyl group on ***t*-BAM**. This hypothesis, however, was ruled out by performing the analogous experiment with **BA**: this led to an equivalent observation (polarizations at $\delta = 5.15$, 5.99, and 6.32 ppm for parent **BA**, Figure 2). Hence, the addition of either **B**$^\bullet$ or **P**$^\bullet$ to an acrylate double bond has to proceed (at least partly) in a reversible way, independent of steric factors.



Scheme 2. Reversible reaction of radicals **B**$^\bullet$ and **P**$^\bullet$ with acrylates, as well as follow-up reactions.

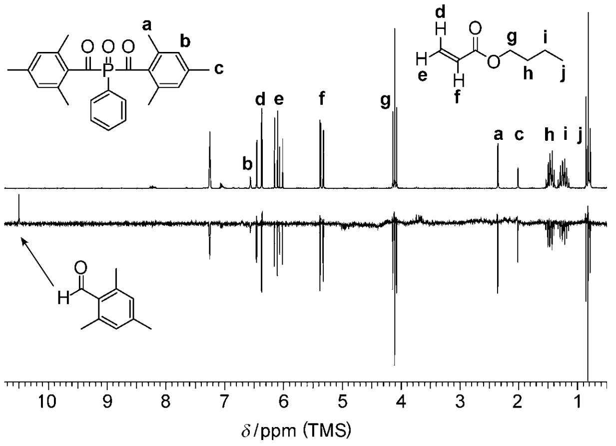


Figure 2. Top: ^{1}H NMR spectrum of **1**/**BA** (1:10) in C_6D_6. Bottom: The corresponding ^{1}H CIDNP spectrum recorded immediately after irradiation.

The second remarkable feature in the ^{1}H CIDNP spectra of **1**/***t*-BAM** and **1**/**BA** (Figures 1 and 2, bottom) is the occurrence of a singlet signal at $\delta = 10.4$ ppm, which is in the characteristic region for an aromatic aldehyde.[27] Clearly, the aldehyde can only originate from benzoyl radical **B**$^\bullet$, but the source of the additional hydrogen atom has yet to be identified. It has been shown that a benzoyl-type radical is able to abstract hydrogen atoms from efficient H donors;[26] however, neither ***t*-BAM** nor **BA** possesses readily abstractable H atoms, and the aldehyde is formed irrespective of the solvent used. To check whether the aldehyde hydrogen atom stems from the reaction of **B**$^\bullet$ with a parent alkene or (even more unlikely) an alternative species, we treated **1** with styrene (**S**), which possesses no abstractable H atoms, under the given reaction conditions. Remarkably, the ^{1}H CIDNP signal at $\delta = 10.4$ ppm is again observed. Thus, the H atom which adds to the benzoyl-type (mesityloyl) radical has to originate from an initially formed radical pair.

An alternative source of the extra H atom could be either of the radicals **BM**$^\bullet$ or **PM**$^\bullet$. Both species are generated at the very beginning of the polymerization and, very likely still carry the polarization of the **B**$^\bullet$/**P**$^\bullet$ radical pair.[30] Hydrogen-atom transfer between **B**$^\bullet$ and **BM**$^\bullet$/**PM**$^\bullet$ would lead to the formation of the observed aldehyde **BH** and alkenes **BM**/**PM** (Scheme 2). Indeed, the ^{1}H resonances around $\delta = 7$ ppm are in accord with these latter molecules (Figures 1 and 2). In all the CIDNP spectra, and even in the presence of a 200-fold excess of alkenes (***t*-BAM**, **BA**, or **S**), the photoinitiator is regenerated as an in-cage recombination product (see the resonances indicated in Figures 1 and 2).

In summary, we have shown that a first (or very early) addition of an initiator radical to an acrylate double bond may occur in a reversible way. Moreover, disproportionation (hydrogen transfer) takes place, which leads to the formation of aldehyde **BH** and phosphine **PH** together with the "new" substituted alkenes **BM** and **PM**. The latter species likely contribute to the polymerization process, even though they are present at a low concentration. It is remarkable that these reactions already arise at the very early stages of the photoinitiated radical polymerizations at room temperature (24 °C), which should be well below the ceiling temperatures of **BA** and **S**, even at low concentrations of these monomers.[31–32] Preliminary experiments indicate that the reversibility of the initial addition step can also be observed upon use of benzoyl peroxide and azobisisobutyronitrile (AIBN). Furthermore, results obtained for **S** (and other monomers) indicate the reversibility of this reaction step.

It is also notable that the parent initiator is regenerated even in the presence of an excess of polymerizable double bonds. This finding indicates that the photoinitiator potentially has activity even at later stages of the polymerization process.

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