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# Phosphorescence Induced by Pressure and Continuous Light Irradiation of Benzophenone and 4,4'-Bis(dimethylamino)benzophenone in Solid Polymers at Room Temperature

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We report efficient room temperature phosphorescence induced by pressure (PIP) and/or by continuous light irradiation (light-induced phosphorescence (LIP)) in two ketones: benzophenone (BP) and its *p*-dimethylamino-substituted (Michler's ketone (MK)) both dissolved in solid poly(ethyl methacrylate) (PEMA). Under pressure both BP and MK reveal a remarkable growth of the phosphorescence intensity: 2 orders of magnitude (within 5 kbar) and 1 order of magnitude (within 50 kbar) respectively for MK and BP. For MK, above 5 kbar the phosphorescence intensity significantly decreases, but for BP the decrease is negligible even above 50 kbar. A model based on the increase of the amount of  $\pi, \pi^*$  character in the predominately  $n, \pi^*$  triplet state with increasing pressure is proposed to account for the observed features of the PIP. The LIP occurs only at pressures below the maximum in the PIP. With prolonged irradiation, the overall shape of the phosphorescence intensity curve versus time depends on pressure, exciting light intensity, and concentration. A tentative explanation of the LIP effect is given that assumes a creation of the phosphorescent photoproduct via the hydrogen abstraction reaction.

## 1. Introduction

In previous papers<sup>1,2</sup> we reported an unusual room temperature phosphorescence induced in 4-(*N,N'*-dimethylamino)benzonitrile (DMABN) dissolved in polymers by pressure (PIP) and an apparently related phosphorescence induced by continuous exposure of the sample to laser radiation of a moderate flux (LIP). For DMABN the LIP depended on several factors including the intensity of the exciting light, the concentration of DMABN in the polymer, and the pressure at which the sample was irradiated.

The PIP intensity increased rapidly with pressure at low pressures, maximized for DMABN near 20 kbar, and then decreased moderately at high pressures. The LIP occurred only at pressures below the maximum in the PIP. At higher pressures under continuous irradiation only a decrease in the PIP intensity with time was observed. At 1 atm the LIP relaxed back to the initial value when the sample was kept in the dark for 10–15 min. However, under pressure (even 3–5 kbar) the LIP was stabilized almost indefinitely.

Because DMABN belongs to the family of so-called twisted intramolecular charge transfer (TICT) molecules (see, e.g., refs 3–6), it seemed reasonable to associate the observed effect with the TICT properties. In the other words, it appeared to us that the LIP and PIP phenomena are unique for TICT molecules that undergo a change in conformation in the excited state. In the case of DMABN, we tentatively ascribed the origin of either the PIP or LIP to the triplet emission of the planar form of the molecule. However, for each process a different pathway for feeding of the “planar triplet” state has been considered. The “twisted triplet” and an unspecified but photochemically created state were postulated as intermediates for the PIP and LIP phenomena, respectively.

In this paper we test some of those hypotheses by comparative studies of two aromatic carbonyl molecules: benzophenone (BP)

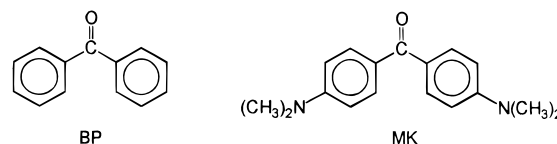


Figure 1. Structure of the BP and MK molecules.

and 4,4'-bis(dimethylamino)benzophenone (BDMABP), commonly known as Michler's ketone (MK) (see Figure 1). The latter is known to be a TICT molecule.<sup>7</sup> The presence of the electron-donating dimethylamino groups and the electron-accepting carbonyl group provides the  $\pi, \pi^*$  transition with some charge transfer character. Moreover, being aromatic carbonyl compounds, BP and MK have both  $n, \pi^*$  and  $\pi, \pi^*$  excitations. Relative to benzophenone, where the  $n, \pi^*$  singlet and triplet states of the molecule are the lowest excited states and the  $\pi, \pi^*$  states are higher in energy, the *p*-dimethylamino substitution in MK decreases the energy of the  $\pi, \pi^*$  states. The relative spectral positions of the  $n, \pi^*$  and  $\pi, \pi^*$  transitions are also significantly medium dependent.

Furthermore, a lone pair orbital of the oxygen atom in both molecules plays an important role in hydrogen bonding and hydrogen abstraction processes. Thus, BP and MK exhibit efficient photoreactivity in many liquids<sup>8–13</sup> and some solid polymers.<sup>14–17</sup> The relationship between the nature of the excited states and the efficiency of photoreduction in hydrogen donor solvents has been of special interest. It has been established that the  $n, \pi^*$  triplet state is highly reactive toward hydrogen abstraction from solvents in comparison with the  $\pi, \pi^*$  triplet state.<sup>18</sup>

In the present paper we further characterize the LIP and PIP phenomena and hope to answer at least two questions: (1) Is it possible to observe the pressure and light-induced effects with other than TICT molecules? (2) What is the role of the  $n, \pi^*$  singlet and triplet states in both effects? It should be noted that although here the results in only one polymeric matrix are presented, very similar behavior was also observed in other polymers.

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## 2. Experiment

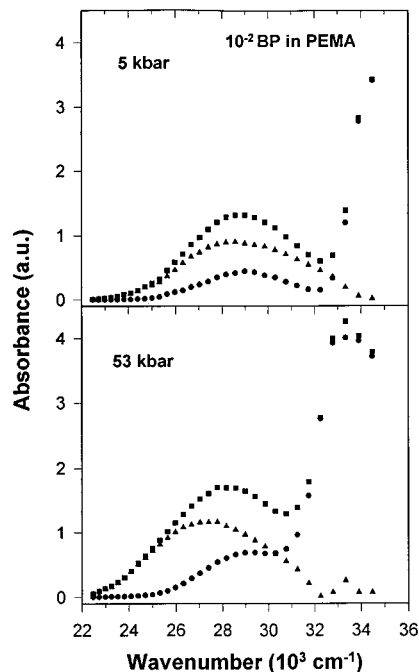
MK (98%) was purchased from Aldrich and purified by triple recrystallization from ethanol (McCormick). BP of 99%+ purity from Aldrich was sublimed twice in vacuum. Both compounds were dissolved in PEMA (poly(ethyl methacrylate) with 250 000 molecular weight) using spectranalyzed methylene chloride as a solvent. In general, a concentration of  $10^{-3}$  mol of MK per mol of monomer unit was employed. In the case of BP, because of the low emission intensity, most of the experiments were performed at a concentration of  $10^{-2}$ . However, in both cases, the concentration dependencies were studied. The sample preparation procedure has been reported in detail before.<sup>1,2</sup> As indicated in ref 2, samples made from solutions thoroughly deoxygenated by bubbling  $N_2$  in a glovebag behaved the same as these prepared in air, so oxygen quenching is not a significant factor in the results.

All of the experiments were performed in a Merrill-Bassett diamond anvil cell (DAC)<sup>19</sup> at room temperature, utilizing modified brilliant cut diamonds with 0.8–1.0 mm culets. The hole diameter of the gasket was approximately 0.3 mm. The application of the DAC to high-pressure luminescence experiments as well as the experimental setup for the luminescence spectra and UV/vis absorption measurements has been described before.<sup>20,21</sup> In the most of the experiments the excitation utilized the 325 nm line of a He–Cd laser in conjunction with various filter combinations. The output laser intensity was estimated to be  $2 \times 10^{16}$  photons/s  $cm^2$ , and the maximum effective intensity at the sample was 2 orders of magnitude lower. (See ref 2 for details.) Almost all the experiments with the 325 nm line were performed with incident intensity about  $7 \times 10^{12}$  photons/s  $cm^2$  unless mentioned otherwise. Occasionally, the 365 nm line of a 200 W mercury lamp with appropriate interference and cutoff filters was used. The incident intensity in this case was estimated to be several times lower than from the laser. During continuous irradiation the emission at the chosen energy was monitored by a single photon counter and computer on line with a reading interval of 1 or 2 s.

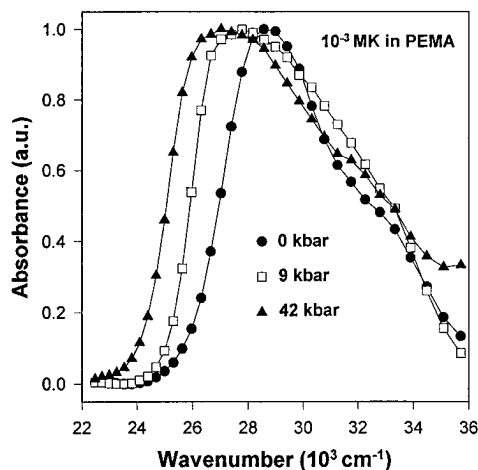
## 3. Results

**3.1. Absorption and Emission Spectra.** At atmospheric pressure the main absorption bands of BP in PEMA are between  $\approx(24\text{--}32) \times 10^3 \text{ cm}^{-1}$  and above  $32 \times 10^3 \text{ cm}^{-1}$ . The first band with a maximum located at  $29.4 \times 10^3 \text{ cm}^{-1}$  (0 kbar) shows a low absorption coefficient and small shift to lower energy with increase of pressure. On the other hand, the high-energy band, of which only the shoulder is seen (because of low UV transmission of the diamonds), exhibits a strong absorption as well as a significant shift to low energy with increase of pressure (see solid circles in Figure 2). Thus, when pressure increases, stronger overlap of the high- and low-energy bands takes place. The pressure dependence of the low- and high-energy bands corresponds to their well-known assignments as an  $n \rightarrow \pi^*$  and a  $\pi \rightarrow \pi^*$  transition, respectively. Under continuous irradiation conditions the  $n \rightarrow \pi^*$  absorption band increases in intensity at all pressures (Figure 2). An intensity increase in  $n \rightarrow \pi^*$  absorption of benzophenone during photoirradiation has also been observed in liquid (e.g., cyclohexane, isopropyl alcohol) (see, e.g., refs 22 and 23) and solid (PMMA, PVA)<sup>15,17</sup> solutions and is attributed to some reaction product having absorption almost coincident with the BP absorption. This light-induced increase in optical density over the entire  $n \rightarrow \pi^*$  region shows little pressure dependence and high stability over a long time.

The emission spectrum of BP in PEMA at room temperature and atmospheric pressure shows a very low emission intensity



**Figure 2.** Absorption spectra of  $10^{-2}$  BP in PEMA at 5 and 53 kbar: (●) before irradiation, (■) after irradiation for 5 min by flux of  $7 \times 10^{12}$  photons/s  $cm^2$ , (▲) difference between before and after irradiation.

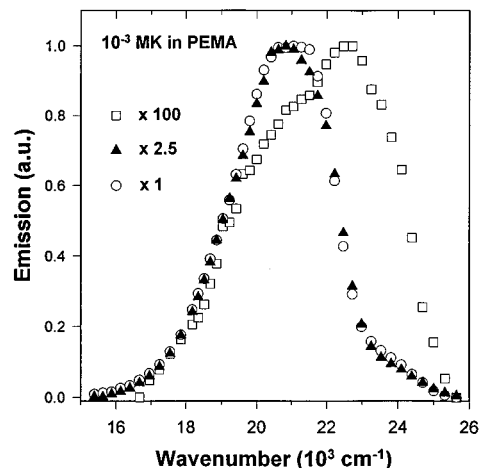


**Figure 3.** Absorption spectra of MK in PEMA at several pressures.

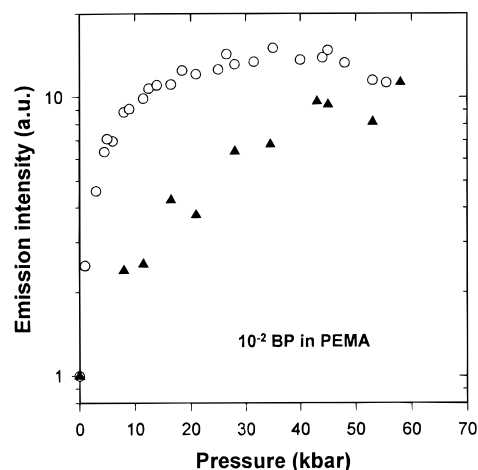
(phosphorescence) with a characteristic vibrational structure. Under pressure as well as under irradiation the spectrum loses its structure and is transformed into a smooth curve with a high intensity and a maximum around  $22 \times 10^3 \text{ cm}^{-1}$ , located at the center of the emission spectrum of the untreated BP.

Figure 3 shows the optical absorption spectrum of MK in PEMA for three pressures. The spectrum at 0 kbar extends from  $24 \times 10^3$  to  $36 \times 10^3 \text{ cm}^{-1}$  and has a peak maximum at  $\sim 28.7 \times 10^3 \text{ cm}^{-1}$  with an absorption shoulder around  $33.5 \times 10^3 \text{ cm}^{-1}$ . With an increase of pressure, the absorption band shifts to the red and has been characterized as consisting of three closely lying electronic states: an  $n\pi^*$  and two  $\pi\pi^*$  states.<sup>24</sup> Continuous irradiation of the sample mainly induces an additional small absorption band below  $24 \times 10^3 \text{ cm}^{-1}$  that is only a little pressure dependent and very stable in time.

Emission of MK in PEMA, at low excitation flux, exhibits a very low intensity and a broad spectrum extended over the region  $16 \times 10^3$  to  $26 \times 10^3 \text{ cm}^{-1}$ . When subject to pressure or moderately high excitation intensity ( $7 \times 10^{12}$  photons/s  $cm^2$ ), the emission intensity of MK in PEMA grows significantly, respectively 100 or 40 times (Figure 4). In the initial spectrum



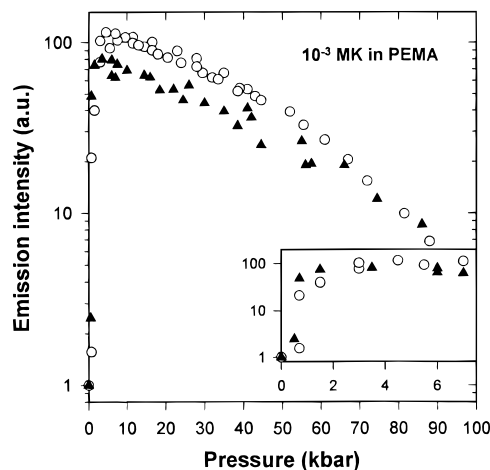
**Figure 4.** Emission spectra of MK in PEMA at 0 ( $\square$ ) and 7 kbar ( $\circ$ ) with excitation intensities lower than  $10^{12}$  photons/s  $\text{cm}^2$  and at 0 kbar ( $\blacktriangle$ ) after continuous irradiation for 5 min with a flux of  $7 \times 10^{12}$  photons/s  $\text{cm}^2$ . Spectra are normalized to the same maximum value. Multiplication factors are 100, 2.5, and 1.0 respectively for ( $\square$ ), ( $\blacktriangle$ ), and ( $\circ$ ).



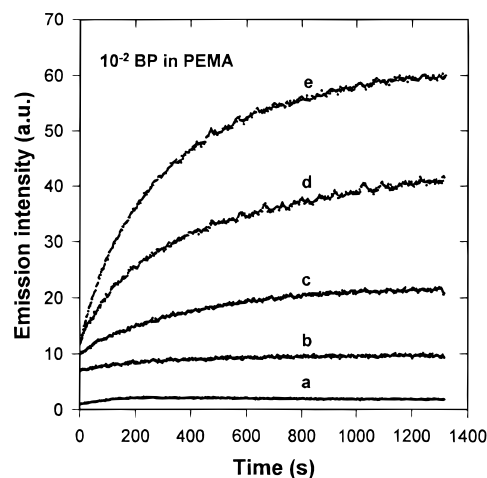
**Figure 5.** Pressure dependence of the relative phosphorescence intensity of BP in PEMA for two excitation lines: ( $\circ$ ) 325 and ( $\blacktriangle$ ) 365 nm. Intensities at atmospheric pressure are normalized to one.

of MK in PEMA, two bands at high and low energy are clearly present; the former is fluorescence and the latter phosphorescence.<sup>24</sup> Because of the growth of the phosphorescence peak, the fluorescence cannot be well distinguished at high pressures. As can be seen from Figure 4, the effect of pressure and of irradiation is primarily to increase the phosphorescence intensity.

**3.2. Pressure-Induced Phosphorescence (PIP).** Since the emission intensities of BP and MK in PEMA change during continuous irradiation, the pressure dependence of the emission intensity has been determined at each pressure on a fresh (not previously irradiated) sample, from the measurements of the intensity at the maximum emission, with a new load for each pressure. This procedure allowed us to minimize the exposure of the sample and thus to avoid any influence of irradiation on the pressure dependency. The results for the pressure effect on the intensity of the main peak (phosphorescence) are presented in Figures 5 and 6 respectively for BP and MK. In the case of BP in PEMA the effect of pressure is a marked increase in phosphorescence intensity that levels at pressures above 50 kbar and then decreases slightly. The pressure effect is much larger for MK than for BP. In the former, the intensity increases rapidly to 5–10 kbar, but then significantly decreases as the pressure is further increased. The relative changes of phosphorescence intensity with pressure are almost independent



**Figure 6.** Pressure dependence of the phosphorescence intensity of MK in PEMA for two excitation lines: ( $\circ$ ) 325 and ( $\blacktriangle$ ) 365 nm. Intensities at atmospheric pressure are normalized to one.

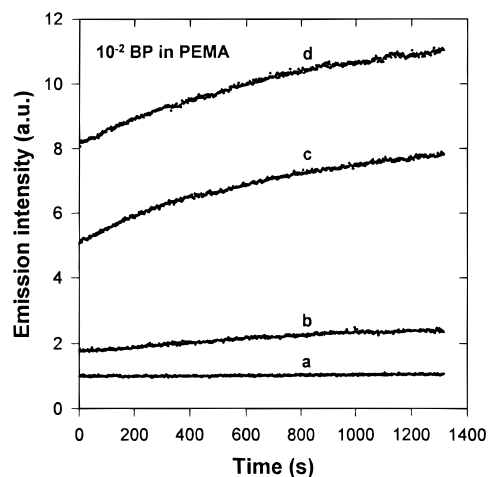


**Figure 7.** Phosphorescence intensity of BP in PEMA under steady-state irradiation conditions for different pressures: (a) 0, (b) 5, (c) 13, (d) 30, and (e) 48 kbar.

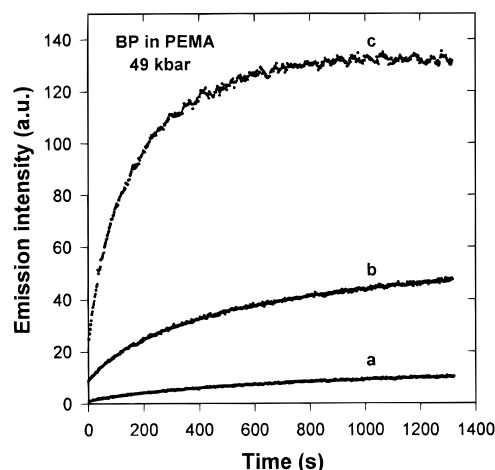
of the excitation line (see Figures 5 and 6). It should be noted that for BP as well as MK significant changes in phosphorescence intensity are accompanied by only a very small shift of the phosphorescence peak position.

**3.3. Light-Induced Phosphorescence (LIP).** Both MK and BP show a significant growth of phosphorescence intensity when exposed to the light of either the laser (325 nm) or mercury lamp (365 nm). Below we present the most characteristic features of the LIP process in PEMA. Although the results are presented only in PEMA, it is worth noting that the LIP phenomenon can also be observed in other polymers.<sup>25</sup>

**3.3.1. BP in PEMA.** In Figure 7 the phosphorescence intensity of  $10^{-2}$  BP in PEMA is shown under continuous irradiation by the 325 nm line of the laser at several pressures. With time of irradiation, regardless of the pressure, the phosphorescence intensity increases gradually from the beginning of illumination and tends to saturate. The higher the pressure, the greater the saturation value that is reached. With the 365 nm excitation line the LIP effect generally shows the same qualitative features as for the 325 nm line. However, as can be seen in Figure 8, the magnitude of the LIP effect is smaller at all pressures, very likely because of the low excitation intensity of the 365 nm line. This is confirmed by experiments with the 325 nm line with additional neutral filters on the excitation. The LIP phenomenon also shows a concentration dependence. It is demonstrated in Figure 9 for three concentra-



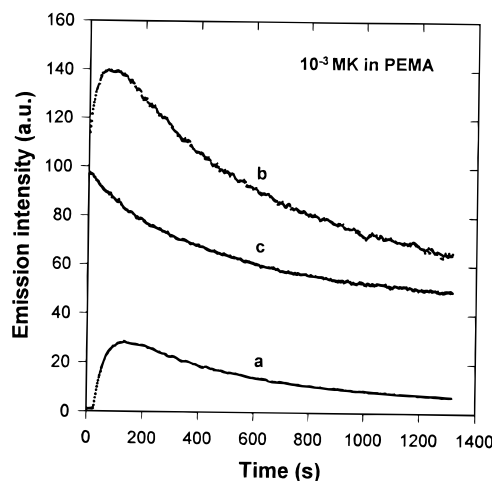
**Figure 8.** Phosphorescence intensity of BP in PEMA under steady-state irradiation conditions for different pressures: (a) 0, (b) 11, (c) 37, (d) 69 kbar. (Note: excitation line 365 nm).



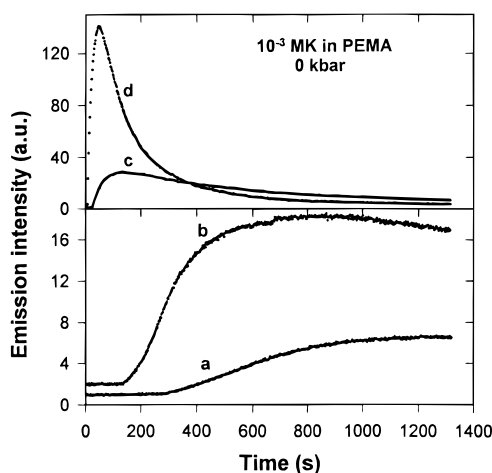
**Figure 9.** Phosphorescence intensity of BP in PEMA at 49 kbar for several concentrations (mol/mol): (a)  $10^{-4}$ , (b)  $10^{-3}$ , and (c)  $10^{-2}$ .

tions of BP in PEMA at 49 kbar. As one can see, the LIP is observed even for  $10^{-4}$  mol/mol, but the slope of the initial rise is greater when the concentration is higher. It should be mentioned that after irradiation the LIP intensity is almost unchanged, even after keeping the sample in the dark for a long time.

**3.3.2. MK in PEMA.** In the case of MK the LIP effect shows additional features besides those observed for BP. In a typical curve (at low pressures), displaying the phosphorescence intensity versus irradiation time, one can distinguish three characteristic regions. This is clearly seen at 0 kbar (Figure 10) where the LIP curve consists of (i) an induction period (IP) during which the initial phosphorescence intensity is almost unchanged (no LIP), (ii) a period of increase with a significant rise of the phosphorescence intensity (LIP), and (iii) a gradual but significant decrease of the phosphorescence emission. With increase of pressure the time evolution of the LIP shows new features. For instance, at 5 kbar when the initial phosphorescence intensity (pressure-induced phosphorescence) is over 2 orders of magnitude higher than at 0 kbar, there is no IP, and the growth of the LIP is much less. At higher pressure (Figure 10, curve c) only a decrease of the phosphorescence intensity is observed over the entire period of irradiation. The overall shape of the LIP curve depends significantly on excitation intensity and concentration of the solute molecules in the polymer. The former effect is presented in Figure 11, at 0 kbar, for two excitation lines and additionally for different excitation



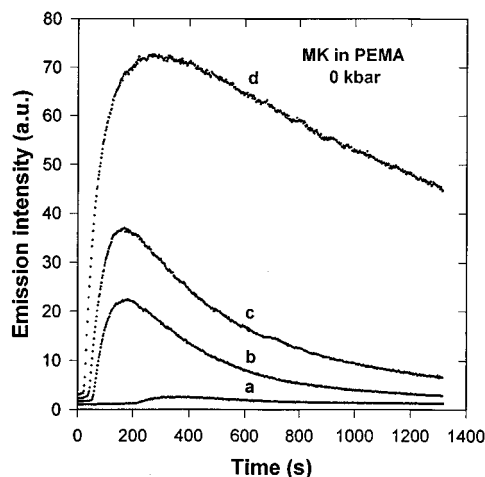
**Figure 10.** Phosphorescence intensity of MK in PEMA under steady-state irradiation conditions at different pressures: (a) 0, (b) 5, and (c) 15 kbar.



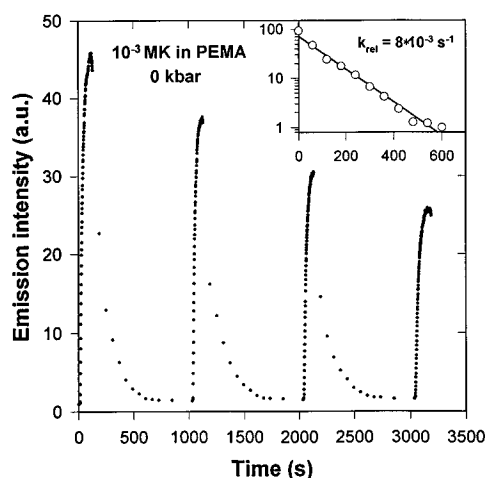
**Figure 11.** Phosphorescence intensity of MK in PEMA under steady-state irradiation conditions at 0 kbar with the 365 nm line (excitation intensity for curve b twice higher than for curve a) and 325 nm line: (c)  $7 \times 10^{12}$  photons/s  $\text{cm}^2$ , (d)  $2 \times 10^{13}$  photons/s  $\text{cm}^2$ .

intensities in each case. As one sees, the stronger the exciting light, the shorter the IP and the steeper the rise of the LIP. The decrease of phosphorescence intensity in the latter part of the emission curve is also larger when the exciting light intensity is higher. An example of the concentration dependence is exhibited in Figure 12. With increasing concentration from  $10^{-4}$  to  $10^{-3}$  the process of inducing the LIP is speeded up as is indicated by shortening of the IP. Moreover, the size of the LIP effect is also enhanced at higher concentrations.

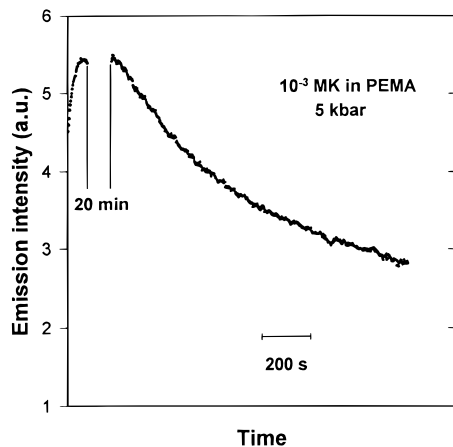
Once irradiated, the sample shows some kind of memory effect. At 0 kbar, it is seen in consecutive runs on the same sample during which the maximum value of the emission intensity does not exceed the final emission value from the previous run (Figure 13). On the other hand, also at 0 kbar, the conditions created during a rise of the LIP have a reversible character. This is documented by decrease of the LIP intensity during each interval when the sample is kept in the dark. In three consecutive runs on the same sample a similar behavior is observed, and the LIP intensity relaxes almost completely within  $\approx 15$  min. The calculated rate constant for this relaxation taken from the first run is estimated to be  $\approx 8 \times 10^{-3} \text{ s}^{-1}$ . This value is obtained from a reasonably good single-exponential fit and is almost independent of the sample history (see following runs). In the sample under pressure, unlike at atmospheric pressure, the conditions created during continuous



**Figure 12.** Phosphorescence intensity of MK in PEMA at 0 kbar for several concentrations (mol/mol): (a)  $10^{-4}$ , (b)  $3 \times 10^{-4}$ , (c)  $5 \times 10^{-4}$ , and (d)  $10^{-3}$ .



**Figure 13.** Phosphorescence intensity of MK in PEMA at 0 kbar under steady-state conditions (rising parts of curve). For the descending part of the curves the sample was excited for approximately 1 s every 1 min. The insert includes the rate of relaxation taken from the first cycle.



**Figure 14.** Phosphorescence intensity of MK in PEMA at 5 kbar under steady-state irradiation conditions including a 20 min interval with no irradiation.

irradiation are very stable in time when sample is kept in the dark. It is clearly seen, for example at 5 kbar, in Figure 14. The previously irradiated sample kept in the dark for 20 min shows an almost unchanged intensity of the LIP. The same high stability of the LIP intensity was detected at all higher pressures where there is an LIP effect, indicating that pressure

stabilizes the irradiation-induced effect. Moreover, at pressures higher than  $\sim 15$  kbar, the decrease of the PIP under continuous irradiation was also very stable for a long time (at least several hours).

#### 4. Discussion

It has been proven that high pressure, acting as a perturbation of the interaction between an individual molecule and its surroundings, can effectively tune phenomena dependent upon the energy levels of excited states (see, e.g., ref 26). Since ketones may apparently possess  $\pi, \pi^*$  and  $n, \pi^*$  triplet states very close in energy, they are of special interest for pressure studies. Solvent studies have shown that the character of the lowest triplet state of BP and MK is highly environmentally dependent. Thus, the change of solvent polarity or external pressure is significantly reflected in some luminescence features of these molecules like intersystem crossing efficiency, phosphorescence efficiency, and photoreactivity of the triplet state toward hydrogen abstraction. However, the processes leading to the change of the character of the lowest triplet state of ketones have not yet been unambiguously determined.

In general, two models have been considered to account for the strong changes in a character of the lowest triplet state of ketones. First, one assumes that two lowest triplet states are energetically close, but each with its own distinctive pure  $n, \pi^*$  and pure  $\pi, \pi^*$  character. The effect of pressure in this case would be a mixing of states of changing dynamic equilibrium between them.<sup>27,28</sup> A second model, more recently introduced and based on benzophenone and cyclophanobenzophenone studies,<sup>29,30</sup> considers, in general, a mixing of the  $n$  carbonyl orbital with the  $\pi$  orbitals of the phenyl rings. Thus, for example, the benzophenone triplet is not a pure  $n, \pi^*$  state because both the  $n$  and  $\pi^*$  orbitals of the carbonyl group are mixed with the aromatic  $\pi$  system. In other words, the triplet has both  $n, \pi^*$  and  $\pi, \pi^*$  character. This mixing is, however, in the sense of configurational mixing (molecular orbital mixing) but not necessarily in the sense of quantum mechanical mixing of well-defined  $n, \pi^*$  and  $\pi, \pi^*$  triplet electronic states. The mechanism of configurational mixing between  $n, \pi^*$  and  $\pi, \pi^*$  states in ketones has been a subject of considerable debate. In benzophenone derivatives, it is thought that out-of-plane twisting of the phenyl rings is responsible for mixing the  $n$  carbonyl with the ring  $\pi$  orbitals, so as to increase the  $\pi, \pi^*$  ( $\pi_{\text{ring}}, \pi^*_{\text{CO}}$ ) character in the lowest triplet state. Since in aromatic ketones the compression of the medium may modify the twist angle of the phenyl rings relative to the carbonyl frame,<sup>30</sup> one would expect a substantial change in the character of the triplet state.

The most striking feature in luminescence of ketones and particularly in the case of BP is the very fast intersystem crossing (ISC). According to the well-known El-Sayed rule, spin-orbit coupling (SOC) is very large and ISC very rapid ( $10^{10}$ – $10^{11}$   $\text{s}^{-1}$ ) only when a change in spin multiplicity is accompanied by a change in electron configuration.<sup>32</sup> Thus,  $n, \pi^* \leftrightarrow n, \pi^*$  and  $\pi, \pi^* \leftrightarrow \pi, \pi^*$  processes are formally forbidden whereas  $n, \pi^* \leftrightarrow \pi, \pi^*$  are allowed. Since the commonly accepted view is that both the  $S_1$  state and  $T_1$  state of benzophenone are  $n, \pi^*$  in character, the apparent violation of these selection rules has attracted much attention. Three possible explanations have been suggested for the  $S_1$  to  $T_1$  ISC: (i) an indirect process involving an intermediate  $\pi, \pi^*$  triplet state which lies below the  $S_1$  and above  $T_1$  ( $S_1[n, \pi^*] \Rightarrow T_2[\pi, \pi^*] \Rightarrow T_1[n, \pi^*]$ ), (ii) a strong vibronic coupling between  $n, \pi^*$  and  $\pi, \pi^*$  states in either the singlet or triplet manifolds,<sup>33</sup> and (iii) a direct mechanism involving the lowest triplet with substantial admixture of the  $\pi, \pi^*$  character ( $S_1[n, \pi^*] \Rightarrow T_1[n, \pi^* + \pi, \pi^*]$ ). The possibility

that  $T_2$  is involved in the ISC process has not been strictly excluded. However, the indirect pathway seems unlikely in light of the fact that no evidence of a  $\pi, \pi^*$   $T_2$  state of BP close in energy to  $S_1$  has been given. The second suggestion is substantiated by the observation that  $S_1$  and  $T_1$  have different C=O stretching and torsional ring mode frequencies. However, it appears unreasonable that the enhanced vibrational overlap which would result from these differences could compensate for the electronically forbidden character of an  $n, \pi^* \leftrightarrow n, \pi^*$  transition. It has been shown that a substantial mixing of  $\pi, \pi^*$  character onto  $T_1$  is capable of breaking down the rule that forbids ISC between states in which there is no one-orbital occupancy change. In the case of BP it has been estimated that the lowest triplet has about 20% of  $\pi, \pi^*$  character.<sup>29</sup> Hence, if the lowest singlet state of BP is a pure  $n, \pi^*$  state, the ISC should be a fast process due to the  $\pi, \pi^*$  character in the triplet state. Moreover, in a series of cyclophanobenzophenone compounds it has been shown that  $\Theta$  (the out-of-plane angle of the carbonyl  $\pi$  system from that of the phenyl rings) is linked to the amount of  $\pi, \pi^*$  character in  $T_1$ . Because the ISC rate,  $k_{ISC}$ , depends on the square of the  $S_1(n, \pi^*)-T_1(\pi, \pi^*)$  matrix element,  $k_{ISC}$  will increase with the extent of  $\pi, \pi^*$  character in the triplet state.

In light of the discussion above, it seems that the model of conformational mixing of the triplet states can best describe pressure dependencies of ketones luminescence. With increase of pressure the degree of  $\pi, \pi^*$  character in the triplet state will increase. The consequences of this increase are the bases for the interpretation of our PIP and LIP results.

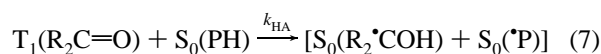
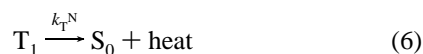
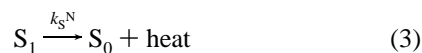
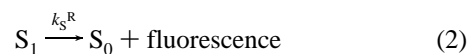
For convenience, the discussion below will be divided in two parts: the pressure-induced effect and the light-induced effect and its pressure dependence.

**4.1. PIP.** The initial phosphorescence intensity of BP and MK in PEMA at room temperature is very low; however, it is about 6 times higher for MK than for BP. Moreover, MK exhibits additionally, at atmospheric pressure, weak fluorescence that is, however, comparable in intensity with the initial phosphorescence. The studies of pressure-induced emission have revealed that both BP and MK exhibit, initially, a remarkable growth of the phosphorescence intensity as the external pressure rises. In addition, the studies reveal the following: (1) the phosphorescence intensity increases within 5 kbar over 2 orders of magnitude and within 50 kbar over 1 order of magnitude respectively for MK and BP; (2) for MK, above  $\sim 5$  kbar the phosphorescence intensity significantly decreases, but for BP the decrease, if any, even above  $\sim 50$  kbar, is negligible; and (3) there is no significant difference in the PIP intensity increase for two different excitation lines (325 and 365 nm).

It is widely recognized that the lowest excited singlet state of BP is  $n, \pi^*$  in character. Relative to BP, the *p*-dimethylamino substitution in MK decreases the energy of the  $\pi, \pi^*$  states. Since the near-ultraviolet region is characterized by an intense absorption band (see Figure 3), it is no longer obvious whether or not the  $n, \pi^*$  state is the lowest excited singlet state. A significant shift toward low energy of the main absorption band with increasing pressure would however indicate a  $\pi, \pi^*$  character for the lowest singlet. This assignment can additionally be supported by two observations: (i) the energy of the fluorescence maximum of MK manifests a pressure shift to lower energy (characteristic for a  $\pi, \pi^*$  state); (ii) a similarity of the pressure effect with that for (dimethylamino)benzaldehyde (DMABA) (see the following paper) where the lowest singlet state is identified as a  $\pi, \pi^*$ . The presence of the electron-donating dimethylamino groups and the electron-accepting

carbonyl group in MK may additionally provide the  $\pi, \pi^*$  transitions with a significant charge transfer character.

The analysis of the pressure effect on the emission intensity of BP and MK is based on a kinetic model which is in principle applicable for both molecules and involves the following primary processes:



Processes 1–6 are typical for monomolecular reactions for either BP or MK but of course with different rates in each case, as will be discussed later.  $S_0$ ,  $S_1$ , and  $T_1$  are respectively the ground state and lowest excited singlet and triplet states. It should be noted, as mentioned above, that  $S_1$  has  $n, \pi^*$  character in BP and  $\pi, \pi^*$  in MK, whereas  $T_1$  in both molecules is predominately  $n, \pi^*$  with some amount of  $\pi, \pi^*$  character, presumably higher in MK than BP.<sup>30</sup> Process 1 describes absorption of the incident light of the  $I_{ex}$  (photons/s cm<sup>2</sup>) intensity with an extinction coefficient  $\alpha$  (cm<sup>-1</sup>). Processes 2, 3 and 5, 6 stand for the radiative and nonradiative decays for the singlet and triplet state, respectively. Process 4 expresses the intersystem crossing from  $S_1$  to  $T_1$ . The rate constants involved in processes from (2) to (6) have their commonly used meaning. Process 7 is responsible for interaction of the triplet state with the polymer. It is assumed that this process involves hydrogen abstraction from the ground state of the hydrogen-containing polymer (PH) with the rate dependent mainly on the amount of the  $n, \pi^*$  character in the triplet state. As a result of this reaction, a ketyl ( $R_2\cdot COH$ ) and macroradical ( $\cdot P$ ) are created in the cage. Some aspects of reaction 7 are presented and discussed in section 4.2.

Fluorescence ( $I_{FI}$ ) and phosphorescence ( $I_{Ph}$ ) intensities under steady state conditions and with a negligible disappearance of the BP and MK molecules in irreversible reactions can be expressed as follows:

$$I_{FI} = \alpha I_{ex} [1 + (k_S^N + k_{ISC})/k_S^R]^{-1} \quad (8)$$

$$I_{Ph} = \alpha I_{ex} [1 + (k_S^N + k_S^R)/k_{ISC}]^{-1} [1 + (k_T^N + \gamma_{HA})/k_T^R]^{-1} \quad (9)$$

where  $\gamma_{HA} = k_{HA}[PH]$  with bimolecular rate  $k_{HA}$  for the hydrogen abstraction reaction.  $[PH]$  is the concentration of the reacting centers of the polymer.

In the case of BP, because of the very rapid ISC, which implies that the  $k_{ISC} \gg k_S^R$ ,  $k_S^N$ , eqs 8 and 9 can be reduced to

$$I_{FI} \approx 0 \quad (10)$$

$$I_{Ph} \approx \alpha I_{ex} [1 + (k_T^N + \gamma_{HA})/k_T^R]^{-1} \quad (11)$$

In the case of MK, eq 9 can be formally rewritten in a form more convenient for analysis:

$$I_{\text{ph}} = I_{\text{fl}}(k_{\text{ISC}}/k_{\text{S}}^{\text{R}})[1 + (k_{\text{T}}^{\text{N}} + \gamma_{\text{HA}})/k_{\text{T}}^{\text{R}}]^{-1} \quad (12)$$

with

$$I_{\text{fl}}(k_{\text{ISC}}/k_{\text{S}}^{\text{R}}) = \alpha I_{\text{ex}}[1 + (k_{\text{S}}^{\text{N}} + k_{\text{S}}^{\text{R}})/k_{\text{ISC}}]^{-1} \quad (13)$$

Equations 10–13 can be the basis for interpretation of the pressure-induced effect. Our experiments indicate that at all pressures  $\alpha I_{\text{ex}}$  was approximately constant. Thus, the pressure dependence of the fluorescence and phosphorescence intensities should follow the pressure changes in the rate constants. Unfortunately, reliable measurements of these rates could not be performed because of the unstable conditions in the sample due to the light-induced effect. Nevertheless, qualitative predictions about pressure dependencies of the involved rate constants can be made.

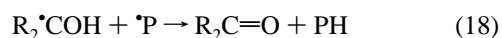
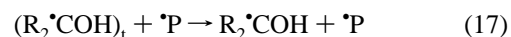
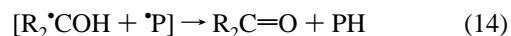
In the case of BP only phosphorescence is observed, and with increasing pressure its intensity gradually increases. As can be seen, eqs 10 and 11 may easily predict that kind of behavior. The lack of fluorescence emission is a natural consequence of the rapid ISC which cannot be changed by pressure due to a strong SOC. A weak phosphorescence intensity at atmospheric pressure may be caused by fast nonradiative processes, i.e.,  $k_{\text{T}}^{\text{N}} + \gamma_{\text{HA}} > k_{\text{T}}^{\text{R}}$ . The increase of pressure should however mix the triplet state, increasing its  $\pi, \pi^*$  character and thus increasing the radiative rate,  $k_{\text{T}}^{\text{R}}$ . As a result of this, the phosphorescence intensity should gradually increase (see eq 11). Additionally, a possible decrease with pressure of the nonradiative rates ( $k_{\text{T}}^{\text{N}}$ ,  $\gamma_{\text{HA}}$ ) due to inhibition of motions of both solute and solvent molecules would also participate in increase of the phosphorescence intensity.

In the case of MK, at atmospheric pressure, there is a low fluorescence and phosphorescence intensity, both of which increase with increasing external pressure. Strictly speaking, the phosphorescence intensity increases very strongly within 5 kbar and then significantly decreases. The pressure dependence of fluorescence intensity could not be determined, because of the strong overlap of the phosphorescence band. However, we believe that, if it would be possible, one would expect to observe an increase of fluorescence intensity with pressure as is found in DMABA (see the following paper). This point will be discussed in the following paper, but here we only would like to mention that an increase of the fluorescence intensity is predicted by eq 8. The primary effect of pressure on the emissive characteristics of MK, as for BP, is the mixing of the triplet state involving an increase in the  $\pi, \pi^*$  character. As a result, two major consecutive effects can be observed. The first is an increase of the radiative rate of the triplet state,  $k_{\text{T}}^{\text{R}}$ . The second effect is a decrease of the ISC ( $k_{\text{ISC}}$ ) due to decrease of the coupling between  $\text{S}(\pi, \pi^*)$  and  $\text{T}(\pi, \pi^* + \pi, \pi^*)$  with an increasing  $\pi, \pi^*$  character in the latter. If  $k_{\text{ISC}}$  decreases with pressure and  $k_{\text{S}}^{\text{R}}$  and  $k_{\text{S}}^{\text{N}}$  are insignificantly pressure dependent, then the left side of eq 13 should also decrease. The phosphorescence intensity is expressed by eq 12 which consists of two factors: one being in front of the square brackets and the other inside them. The former factor is independently expressed by eq 13 and will, as pointed out above, decrease with pressure. On the other hand, the expression in brackets will decrease with increasing pressure due to the rapid increase of  $k_{\text{T}}^{\text{R}}$  and the decrease of  $\gamma_{\text{HA}}$  (slowing down of the hydrogen abstraction reaction). If the increase of  $k_{\text{T}}^{\text{R}}$  is larger than decrease of  $k_{\text{ISC}}$ , then eq 12 would simulate an experimentally obtained dependence of  $I_{\text{ph}} = f(p)$  with its characteristic strong

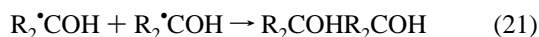
low-pressure increase and high-pressure decrease. (See the following paper for a more quantitative treatment.)

**4.2. LIP.** With prolonged exposure to the light, either laser or mercury lamp, BP and MK develop a strong new emission. A relatively low rate of the buildup step and then a high stability of the changes created in either emission or absorption indicate clearly that these compounds, under continuous irradiation, participate in photoreactions in polymeric media. As a result of these reactions, new entities are produced and almost nonphosphorescent compounds become efficient organic phosphors at room temperature. The processes leading to that kind of transformation seem to be complex, but, we believe, four general steps concerning new entities can be distinguished: (i) photochemical generation, (ii) ground state relaxation, (iii) excitation, and (iv) decay of the excited state. Below we discuss some possible scenarios for the above processes.

The photochemistry of ketones in general and benzophenone in particular has been very thoroughly studied. Of special interest has been the reactivity of these molecules in the lowest  $n, \pi^*$  triplet state. In this state the molecule can undergo  $\alpha$  cleavage, charge transfer complexation, or hydrogen abstraction. For benzophenone-type molecules the hydrogen abstraction process has been widely accepted as the prevailing process. Most of the previous works have concentrated on liquid solutions. There are only a few examples of ketone reactions in solid polymers.<sup>14–17</sup> In contrast to liquids, it has been suggested that hydrogen abstraction, in a polymer below its glass transition temperature ( $T_{\text{g}}$ ), proceeds mainly from a higher  $n, \pi^*$  triplet state, i.e., in a two-photon process. Since our effective excitation flux is over 2 orders of magnitude lower than employed by Brauchle et al.,<sup>15</sup> who proposed a two-photon process in their holographic photochemistry with benzophenone in poly(methyl methacrylate), it seems to us that biphotonic process is probably not a predominant path for creation of radicals in our light-induced effect. However, at this stage of investigations, from our steady-state measurements, we are unable to answer this question conclusively. For the purpose of the further discussion we assume that hydrogen abstraction reaction starts basically in a one-photon process from the lowest triplet state. In the polymer matrix, where diffusion of the solute is highly restricted, interaction between solute and solvent is limited to the closest surroundings. Therefore, the cage and geminate effects are proposed to play an important role in the hydrogen abstraction process in the solid media.<sup>34</sup> In the primary step of this process a cage–radical pair is assumed to be formed (see reaction 7). The rate coefficient for this reaction ( $k_{\text{HA}}$ ) is governed by such factors as the amount of the  $n, \pi^*$  character in the triplet state, the strength of the C–H bond in the hydrogen donor, and distance and orientation between ketone and the donor molecule. Secondary steps of the hydrogen abstraction take place in the ground state and may in general include the following processes:







Processes 14 and 15 concern the effects in the cage where a geminate pair of the radicals may undergo recombination or separation. The latter process is understood to involve a short distance of separation, supposedly due to reorientation of the two fragments of the geminate pair with respect to each other. Furthermore, the ketyl radical may be trapped (16) in the proximity of the polymer radical and later released from the trap (17) to recreate the original molecules (18) or to create an adduct (19) between them. Processes 20 and 21 concern, in turn, the secondary hydrogen abstraction (from the ketyl radical) and dimerization of the ketyl radicals. In view of the highly restricted diffusion in the polymer the last two processes are of minor importance. The preferred final product of the reactions from (14) to (21) depends upon the relative rate coefficients of these processes and may vary appreciably from system to system. In the systems studied, only trapped ketyl radicals and/or an adduct of the polymer and solute can be considered as potential participants in the light-induced effect. In order to interpret our results, we assume that the above entities are the source of the light-induced phosphorescence. (We call it also a phosphorescent photoproduct.) In the view of this model the excited radicals and/or adducts should give an efficient phosphorescence emission. Moreover, under continuous irradiation, the temporal evolution of the LIP curve would basically reflect a change in the concentration of the light created entities. The excitation of these entities could proceed in two different ways: (1) by direct absorption of the exciting light or (2) by triplet-triplet<sup>35</sup> energy transfer between the original molecule and the phosphorescent photoproduct. Since the latter mechanism operates at short distances ( $\sim 1$  nm) due to its exchange character,<sup>36</sup> while even at  $10^{-2}$  mol/mol, the distance between solute molecules is  $\sim 3-4$  nm, assuming uniform distribution of the solute in the polymer, it seems unlikely that the conditions for the exchange mechanism are fulfilled. On the other hand, there is evidence, especially for BP (see Figure 2), that new, light-induced, absorption appears in the energetic region accessible for our exciting light. This spectral change, among others, has been attributed<sup>16,17</sup> to the absorbing ketyl radical and polymer-BP adduct. On the basis of the above, in the case of BP, one can suggest the following scenario for the LIP effect: (i) continuous irradiation produces trapped ketyl radicals and/or polymer-BP adducts, (ii) direct absorbed light raises the entities to their excited state, (iii) decay to the ground state is highly radiative phosphorescence which energetically coincides with that for BP. With prolonged irradiation the curve of the LIP intensity (see Figure 7) increases at a slower and slower rate, indicating that photochemical conversion of BP molecules into phosphorescent photoproduct approaches saturation. Higher intensity as well as higher concentration should speed up the process. In fact, this is seen in Figure 7 versus Figure 8 (excitation light intensity effect) and in Figure 9 (concentration effect).

In the case of BP, the effect of pressure on the light-induced phenomenon could be twofold: (i) a decrease of the hydrogen abstraction reaction as a result of decreasing  $n, \pi^*$  character in the lowest triplet state of the BP molecule and (ii) an increase of  $\pi, \pi^*$  character in the triplet state of the photoproduct molecule. Moreover, if one assumes that the pressure coefficient for change in the character of the triplet state is larger for the photoproduct molecule than for the BP molecule, then the increase of pressure would enhance the intensity of the light-induced phosphorescence. This effect can be seen in Figure 7,

where the LIP intensity, very small at atmospheric pressure, increases significantly with increasing pressure. It is also noteworthy that the time at which the LIP intensity maximizes, increases with increasing pressure very likely indicating a decrease of the hydrogen abstraction reaction. A decrease of the hydrogen abstraction reaction with pressure should also be reflected in the absorption spectra. Surprisingly, absorption in the excitation region does not decrease but even increases (Figure 2). This is, perhaps, due to another species that absorbs in this region and/or an increase of absorption coefficient of the phosphorescent photoproduct with increasing pressure. It is believed that the above effects could mask a real correlation between absorption coefficient and amount of the light created entities that participate in the LIP.

The explanation of the LIP effect given above for BP applies also, we believe to MK. However, several new features in the LIP curve indicate that additional processes are involved. Basically, for MK the overall processes are more pronounced than for BP and DMABN.<sup>2</sup> In the latter case, however, the same tendencies have been observed as for MK but with much lower efficiency. First, at atmospheric pressure, the LIP effect exhibits the highest growth and also the highest degree of reversibility. The reversibility of the LIP effect can be understood as a reversion to the initial molecules (solute, solvent) from the light-induced entities. Since this process can be completed within minutes (see Figure 13), it would indicate a limited stability of these entities at 0 kbar. If the trapped MK radical and adduct between MK and polymer are the primary entities, they should undergo escape from the trap and then recombination in the first case and dissociation in the second case. The former process seems to be more rational; the latter, however, could be possible if one assumes that adduct is rather an associate of the radical molecule and radical polymer than a well-bonded complex of two radicals. With increasing pressure the reproduction process is drastically slowed down and extends from minutes to many hours or even days (see Figure 14). It is believed that increase of pressure decreases mobility of the polymer as well as the solute and thus increases the internal barrier between radicals and macroradicals.

In contrast to BP, the LIP intensity in MK is not enhanced with pressure but strongly reduced (see Figure 10). This pressure effect can be explained if one assumes that the lowest triplet state of the product molecule, in contrast to the parent molecule, has primarily  $\pi, \pi^*$  character. Thus, at atmospheric pressure the LIP intensity is high, but with increasing pressure it reduces due to a decrease in the overall hydrogen abstraction reaction (primary and secondary processes).

In the case of MK as well as DMABN there is a pronounced induction period before the light-induced effect accelerates suddenly. Suppan,<sup>10</sup> who observed a similar effect on MK absorption in cyclohexane, suspected the presence of impurities in the sample, in particular, oxygen. Since the degassed sample<sup>2</sup> shows the same IP as an untreated sample, it is unlikely that oxygen is involved in this process. However, it seems to us that presence of the IP is determined by some kind of quenching process which involves the triplet state. The lack of the IP in BP is probably explained by the significantly shorter lifetime of the relative triplet in BP than MK.

Another important characteristic of the LIP effect of MK is a decrease in phosphorescence intensity with time of irradiation. At all pressures for shorter times it is masked by the rise in intensity due to creation of the phosphorescent photoproduct, but at higher pressures when no phosphorescent product is produced it appears as soon as the irradiation starts. The decrease is highly irreversible even at atmospheric pressure and

depends only moderately on concentration or pressure. Since no similar degradation phenomenon is observed in BP, it must be associated with a charge transfer excitation. It occurs at pressures above those in which the phosphorescent photoproduct is produced so it must involve a different pathway via either the original excited singlet or triplet. We have not been able further to characterize the reaction or identify the product. In the following paper we demonstrate a similar effect in the substituted aldehydes.

## 5. Conclusions

We have shown that pressure- and light-induced effects, which we first thought to be characteristic for TICT molecules, are also observed in a non-TICT molecule. For BP and MK, the PIP and LIP effect is governed by the  $n,\pi^*$  character of their lowest triplet state. The PIP is proposed to be caused by pressure mixing of the triplet state involving an increase its  $\pi,\pi^*$  character. The change in the phosphorescence emission is a result of two consecutive effects: (1) an increase of the radiative rate of the triplet state and (2) a decrease of the intersystem crossing rate (in the case of MK). The LIP is assumed to occur as a result of the hydrogen abstraction reaction of the  $n,\pi^*$  triplet state with the polymer, leading to efficient phosphorescence associated with a phosphorescent product produced. The apparent coupling between PIP and LIP takes place through the  $n,\pi^*$  character of the lowest triplet state.

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