Effect of Pressure and Radiation on the Luminescent Properties of Poly(vinylbenzophenone−styrene)[†]

G. Yang, Z. A. Dreger,[‡] and H. G. Drickamer*

School of Chemical Sciences, Department of Physics and Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801

Received: January 27, 1997; In Final Form: March 12, 1997

High-pressure luminescence studies have been made on a polymer with a polystyrene base but with every seventh styrene converted to benzophenone (BP). The polymer was studied neat (PVBS) and in a 10% solution in polystyrene (PVBS−PS). As for BP dissolved in polymers, both photophysical and photochemical effects are observed originating from the triplet state (T_1). For PVBS, in addition to the phosphorescence from the monomer, an emission at lower energy occurs which we identify as an excimer and some emission at higher energy identified as delayed fluorescence. In PVBS−PS there is little or no excimer but more intense delayed fluorescence. For PVBS the strongest photophysical effect occurs in the first few kilobar where the excimer intensity increases by a factor of 3−4 at the expense of the monomer phosphorescence. At higher pressure both emissions decrease. For PVBS−PS the phosphorescence (measured on its low-energy side) shows first a modest increase and then a decrease, analogous to the behavior of BP dissolved in polymers. The delayed fluorescence decreases significantly with increasing pressure. The major effect of irradiation is the dramatic growth of a new emission 4000 cm^{-1} below the monomer phosphorescence. We attribute this to an emitting photo product much like that observed for BP dissolved in polymers but shifted strongly to lower energy. This occurs in both PVBS and PVBS−PS. The intensity of this emission decreases with increasing pressure. A second effect of irradiation is the strong decrease in the delayed fluorescence, which we attribute to the decreased availability the original phosphorescence for $T_1 \rightarrow S_1$ back-feeding.

Introduction

In a series of papers[1−5] from this laboratory we presented and discussed the photophysics and photochemistry of the triplet state of aromatic carbonyls—nitriles, aldehydes, and ketones—primarily dissolved in polymeric media. In this paper we exhibit and discuss the effect of pressure on the emission from a polystyrene-based polymer in which about one in seven styrenes has been converted to benzophenone, with the BP presumably randomly distributed along the vinyl chain poly-(vinylbenzophenone−styrene) (PVBS).

The previous papers discussed the rather extensive relevant literature on these carbonyls dissolved in liquids or polymers and studied at atmospheric pressure. In this paper we primarily compare and contrast the behavior of PVBS neat and dissolved at 10% concentration in PS (PVBS−PS) with each other and with previous high-pressure data on BP dissolved in polymers. References to atmospheric pressure studies are included only where they are directly relevant to the interpretation of the present study.

Our previous work on BP involved the molecule dissolved in poly(ethyl methacrylate) (PEMA) or poly(vinyl chloride) (PVCl) at a concentration of 10^{-2} mol/mol of monomer, as well as the crystalline solid BP. BP dissolved in PS at this concentration yielded rather weak emission even at high pressure which was somewhat difficult to analyze quantitatively; however, both the photophysics and photochemistry were quite similar to that observed for BP dissolved in PVCl. Even at higher concentrations (5×10^{-2}) neither the emission at

$\sim$18 000cm^{-1} nor that at 25 600 cm^{-1}, major features of the present study, was observed.

As in our previous work, we perform the experimental work in a manner that separates the photophysics (the "pure" pressure effect) from the photochemical effects (the effect of continuous radiation at constant pressure).

Since we use many of the arguments developed for BP dissolved in polymers in this paper, it is desirable to review briefly the concepts obtained from our previous work. In the analysis of the photophysics of BP dissolved in polymers, the intensity of phosphorescence was assumed to depend on (a) the rate of intersystem crossing from S_1 to T_1, (b) the radiative rate from the triplet state, (c) the nonradiative rate from the triplet, and (d) the chemical reactivity of the triplet. Because of the short times involved in measuring the pure photophysical effect, factor d could be neglected in analysis of the photophysics.

Based purely on spin−orbit interactions, k_{ISC}, the intersystem crossing rate should be determined by the difference in $\pi−\pi^*$ and $n−\pi^*$ content of S_1 and T_1 (El-Sayed's rule). However, factors such as vibrational coupling of the S_1 and T_1 potential wells must be significant since for BP the intersystem crossing is very fast ($\sim$10^{12} s^{-1}) although S_1 is essentially all $n−\pi^*$ and T_1 is 80−85% $n−\pi^*$ at 1 atm.

Since $\pi−\pi^*$ excitations are always stabilized by compression and $\pi−\pi^*$ emissions are much more efficient than $n−\pi^*$, one could anticipate, on the basis of this consideration, an increase in phosphorescence efficiency with pressure, and in many circumstances this was observed. The nonradiative rate from T_1 can increase with a shift to lower energy of T_1 with respect to S_0 (the energy gap law) or due to increased coupling to the medium with compression. In crystalline BP the coupling is strong initially and increases with pressure, so only a decrease in emission intensity with pressure was observed.

The photochemistry observed in the studies of dissolved BP

Luminescent Properties of PVBS—PS

J. Phys. Chem. B, Vol. 101, No. 21, 1997 **4219**

and its derivatives involved two processes: (1) Hydrogen abstraction and production of a new emitting (phosphorescent) product that might or might not coincide in energy with the original phosphorescence, this process being reversible at 1 atm but irreversible at even a few kilobar; (2) the excitation to T_2 and a subsequent irreversible reaction to nonemitting products.

As discussed below, in the polymers studied here additional processes were observed. We can however use in a qualitative way some of the concepts outlined above.

Experiment

Poly(vinylbenzophenone—styrene) (PVBS) was synthesized by benzolation of polystyrene (PS) in our lab according to the method of ref 6. PS (average MW 250 000), benzoyl chloride (99%), and aluminum chloride (99.99%) were purchased from Aldrich and used without further purification. The ratio of PS and benzoyl chloride was controlled in the reaction to give a copolymer with a ratio of vinylbenzophenone to styrene of 15:100. The ratio of vinyl benzophenone and styrene in the copolymer was determined by the UV absorption spectrum of the copolymer solution in methylene chloride and used benzophenone solution as a reference.

The PVBS was dissolved in methylene chloride (spectral grade), and the solution was then poured in a glass dish to form a transparent film after the solvent evaporation at room temperature. The optically clear film obtained then was placed in a vacuum oven for a few days at 45 °C. The sample of PVBS (10%) in PS was obtained by the same process, using a solution with 22 mg of PVBS and 200 mg of PS. The thicknesses of the samples were 50−80 μm.

All of the experiments were performed in a Merrill-Bassett type diamond anvil cell (DAC), utilizing low fluorescent and UV transmitting diamonds. The hole diameter of the gasket was approximately 0.3 mm. The sample and a tiny ruby chip were placed in the hole and light mineral oil was used as hydrostatic medium. The pressure was determined by the ruby fluorescence shift.[7] The application of the DAC to high-pressure luminescence experiments as well as the experimental setup for the luminescence spectra has been described before.[8,9] The excitation was by means of the 325 nm line of a Model 3056 Omnichrome Inc. He−Cd laser in conjunction with various filters to cut extraneous radiation from the emission path and to control the intensity of the excitation light. The emission at the chosen energy was measured by a single photon counter and computer on line with a reading interval of 1 or 2 s. For the measurement at 82 K, a variable temperature cryostat (Model DET-418-CVT) was employed. Liquid N_2 was used as the coolant, and the temperature was displayed and controlled by a 320 Autotuning temperature controller (Lake Shore).

As discussed in our previous work on benzophenone dissolved in various polymers, in addition to the photophysical process (phosphorescence) photochemistry also occurs. To separate these processes and to obtain the effect of pressure on the photophysics (the "pure" pressure effect), spectra were first obtained at various pressures to locate the photoluminescence peak (or peaks). Then on a fresh load the intensity was measured at the peak energy, a process involving exposure for 3−4 s. A new load was used for each pressure using gaskets carefully selected for uniformity of the hole.

Results

Figure 1A,B presents the spectra of PVBS polymer and of this polymer at 10% concentration in PS at 5 and 20 kbar at room temperature (298 K). The emission at 22 000−23 000 cm^{-1} is the phosphorescence observed for BP dissolved in
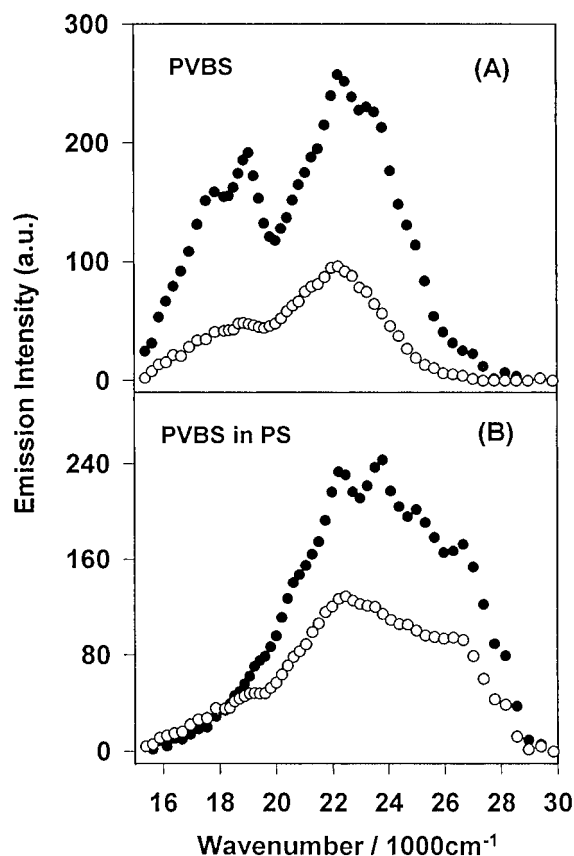

Figure 1. Emission spectra of the polymer PVBS and PVBS (10%) in PS at different pressures. (A) PVBS: (●) 5 kbar, (○) 20 kbar. (B) PVBS (10%) in PS: (●) 5 kbar, (○) 20 kbar.

various polymers[2,4,5] with considerable overlap from the delayed fluorescence as discussed below. In addition, there is significant emission in the region 17 000−19 000 cm^{-1} and at 25 000−26 000 cm^{-1}. The low-energy emission is much more intense in PVBS than for the polymer dissolved in PS (PVBS−PS). The inverse is true for the high-energy emission. In order to characterize these features better, we measured 1 atm spectra at 298 and 82 K (Figure 2A and 2B). Since each of these spectra involved a different loading of the DAC and different degrees of radiation effects, the comparisons can best be made by expressing the intensities at a given T and P (temperature and pressure) relative to the intensity at 22 200 cm^{-1} (450 nm) at that P and T (the center of the phosphorescence). These results are presented in Table 1, the upper half comparing the effect of temperature and the lower half comparing the effect of pressure at 5 and 20 kbar at 298 K. In the discussion we use PVBP for the neat polymer and (PVBP−PS) for the polymer dissolved in PS.

It must be kept in mind that the delayed fluorescence emission overlaps strongly with the phosphorescence,[10] and thus the changes in intensity at 22 200 cm^{-1} (450 nm) with temperature and pressure may, to a considerable degree, be due to changes in delayed fluorescence intensity as well as to effects primarily of the phosphorescence. This is particularly true for PVBS−PS where the delayed fluorescence at 298 K is relatively strong.

In addition to the expected sharpening of the vibrational components of the phosphorescence at 82 K, there are two features which stand out for the temperature effect. At 25 000−26 000 cm^{-1} the emission intensity, which is much stronger in PVBS−PS than for PVBS, at 298 K disappears for both materials at 82 K. This, together with its energy, is a strong indication that it is delayed fluorescence induced by feeding from T_1.
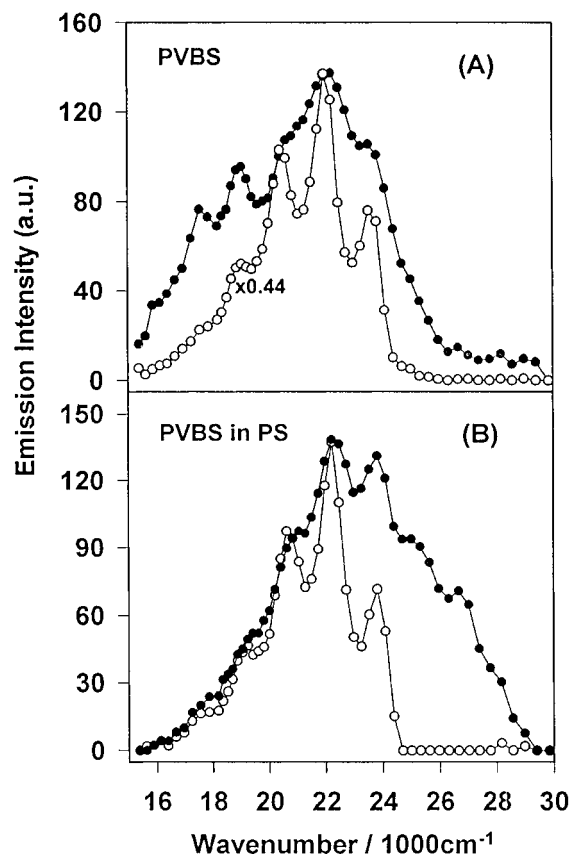
Figure 2. Emission spectra of the polymer PVBS and PVBS (10%) in PS at different temperatures: (A) PVBS: (•) room temperature (298 K), (○) 82 K. (B): PVBS (10%) in PS: (●) room temperature (298 K), (○) 82 K.

TABLE 1: Intensity at Various Energies Relative to the Intensity at 22 200 cm^{-1} (450 nm)

	25 640 cm^{-1} (390 nm)	25 000 cm^{-1} (400 nm)	18 800 cm^{-7} (550 nm)	17 860 cm^{-1} (560 nm)
PVBS (298 K, 1 atm)	0.21	0.34	(0.62)^b	(0.54)^b 0.12
PVBS (82 K, 1 atm)	0.01	0.03	0.34	0.13
PVBS−PS (298 K, 1 atm)	(0.61)^b 1.0	(0.67)^b	0.26	0.17
PVBS−PS (82 K, 1 atm)	0.00	0.00	0.24	0.13
PVBS (298 K, 5 kbar)	0.24	0.44	0.75	0.54
PVBS (298 K, 20 kbar)	0.08	0.19	0.53	0.18
PVBS−PS (298 K, 5 kbar)	0.72	0.85	0.24	0.17
PVBS−PS (298 K, 20 kbar)	0.72	0.76	0.30	0.13

^{a} PVBS = neat polymer; PVBS−PS = 10% polymer in PS. ^{b} The effects of radiation are very strong at these wavelengths so that the ratios taken from the spectra (shown in parentheses) cannot be used in interpreting trends. When available, the ratios taken from the pure photohysical measurements are shown.

In the energy region 17 000−19 000 cm^{-1} it is difficult to interpret the relative intensities at 1 atm because of the strong radiation effects. (See footnote in Table 1.) However, from the results at 5 and 20 kbar where the radiation effect is less significant, it is clear that the relative intensity in this spectral region is considerably greater for PVBS than for PVBS−PS. As discussed below, we interpret the emission in this region as a combination of excimer emission with the 0−3 and 0−4 bands of the monomer phosphorescence. It is not unreasonable that there is significant excimer emission for PVBS while for
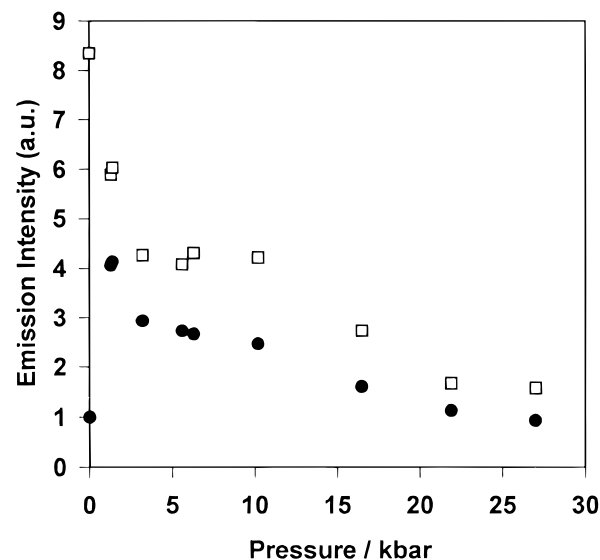

Figure 3. Pure pressure effect on the emission of PVBS: (●): detected at 560 nm (17 900 cm^{-1}); (□) detected at 450 nm (22 200 cm^{-1}).
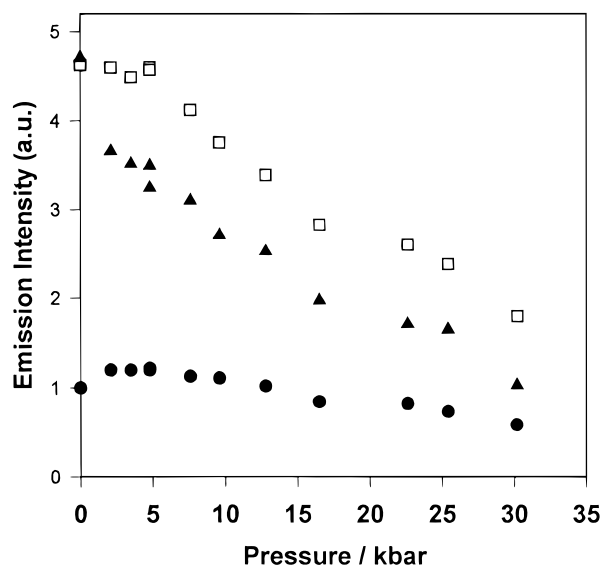

Figure 4. Pure pressure effect on the emission of PVBS (10%) in PS: (●) detected at 500 nm (20 000 cm^{-1}); (□): detected at 450 nm (22 200 cm^{-1}); (▲): detected at 390 nm (25 600 cm^{-1}).

PVBS−PS there is little if any. The larger delayed fluorescence intensity for PVBS−PS can, in part, be associated with the smaller amount of excimer formation.

From the lower half of Table 1 plus the 1 atm data at 298 K, we see that, by and large, there are only modest changes in relative intensity with pressure above 5 kbar at 298 K. The decrease in the relative amount of delayed fluorescence at 20 kbar for PVBS may be real as is possibly the increase in relative intensity for PVBS−PS at low energy. It must be kept in mind that there are photochemical effects that differ with pressure and emission energy as discussed below, so that it is necessary to avoid overinterpreting moderate differences at different pressures.

Since it takes several minutes to measure spectra such as those in Figures 1−4, they undoubtedly involve some photochemistry as well as photophysics. We therefore separate the photophysical effects (the "pure" pressure effects) by the technique described under experiment as well as in previous papers.[1−5] The pure pressure effects are exhibited in Figures 3 and 4 for PVBS and PVBS−PS.

For PVBS (Figure 3) at 450 nm (22 200 cm^{-1}) there is an

Luminescent Properties of PVBS−PS

J. Phys. Chem. B, Vol. 101, No. 21, 1997 **4221**

initial sharp drop in intensity by a factor of over 2 in 1−2 kbar, then a leveling, and a further drop by a factor of over 2 from 10 to 27 kbar. At 560 nm (17 900 cm^{-1}) the intensity shows an initial steep increase by a factor of ~4 over the range 1−2 kbar and then a decrease which accelerates above ~10 kbar. We shall elaborate on the relationship between these two emissions in the Discussion section. At 390 nm (25 640 cm^{-1}) the emission was too weak for quantitative measurement of the pure pressure effect.

Figure 4 exhibits the pure pressure effect for PVBS−PS at three energies. At 390 nm (25 640 cm^{-1}) the emission is very largely due to delayed fluorescence. At 500 nm the emission is primarily monomer phosphorescence. At 450 nm (22 200 cm^{-1}) there is a mixture of monomer phosphorescence and delayed fluorescence. The emission at 550−560 nm is too weak to permit quantitative measurements of the pure pressure effect. The high- energy emission intensity (delayed fluorescence) drops 25% in 1−2 kbar and then exhibits a more gradual continuous decrease by a factor of 2−3 by 30 kbar. The emission at 500 nm (monomer phosphorescence) displays a modest increase in intensity to ~5 kbar and then decreases by a factor of about 2 by 30 kbar. The emission at 450 nm (22 200 cm^{-1}) shows a combination of the behavior of the low- and high-energy emissions. The sharp drop at HE and the modest rise at LE combine to give an intensity independent of pressure to 5 kbar. Then there is a continuous drop by a factor of 2−2$^1/_2$ to 30 kbar.

In addition to the photophysical effects presented above, there were photochemical effects in a number of ways analogous to those observed for BP dissolved in various polymers. Some examples of the effects of 22 min irradiation at various wavelengths are exhibited in Figure 5A,B for PVBS and in Figure 6A, B for PVBS−PS. The more striking effects are (1) from Figure 5B the increase by nearly an order of magnitude in the intensity of emission at 560 nm (17 900 cm^{-1}) for PVBS at 1 atm, and (2) the increase of emission intensity by a factor of ~3 after a short delay time for PVBS−PS at 1 atm and 550 nm (18 200 cm^{-1}) (Figure 6B). At 450 nm (22 200 cm^{-1}) the increase is only ~30%.

In Figure 7A,B B the spectra of PVBS before and after 22 min irradiation at 5 and 20 kbar are shown. Figure 8A,B displays the results of similar measurements for PVBS−PS.

There was, as noted previously, some radiation effect while taking the "before radiation" spectra. It was not possible to get spectra at 1 atm after irradiation since the process is reversible there. In all cases there is an increase in intensity at ~18 000 cm^{-1} (550−560 nm) relative to that ~22 200 cm^{-1} (450 nm). This is particularly evident in Figure 7A.

Table 2A summarizes the radiation results as taken from Figure 5 and 6, and similar radiation studies not shown. Table 2B shows analogous data taken from the spectra of Figures 7 and 8. As can be seen, the internal consistency for the data from the two types of measurements is high. It can also be seen that the intensity at 550−560 nm (~18 000 cm^{-1}) always increases after radiation relative to the intensity at 450 nm (22 200 cm^{-1}), while the intensity at 390 nm (25 640 cm^{-1}) always decreases. We elaborate on these results in the Discussion section.

For aromatic carbonyls dissolved in polymers, where significant growth in emission intensity with irradiation time was observed at 1 atm, the process was reversible with a relaxation time of (6−25) × 10^{-3} s^{-1}.[1−3,5]

In Figures 9 and 10 we exhibit the reversibility of the irradiation increase at 1 atm. In Figure 9 we compare the relaxation in PVBS and in PVBS−PS at ~18 000 cm^{-1} (560
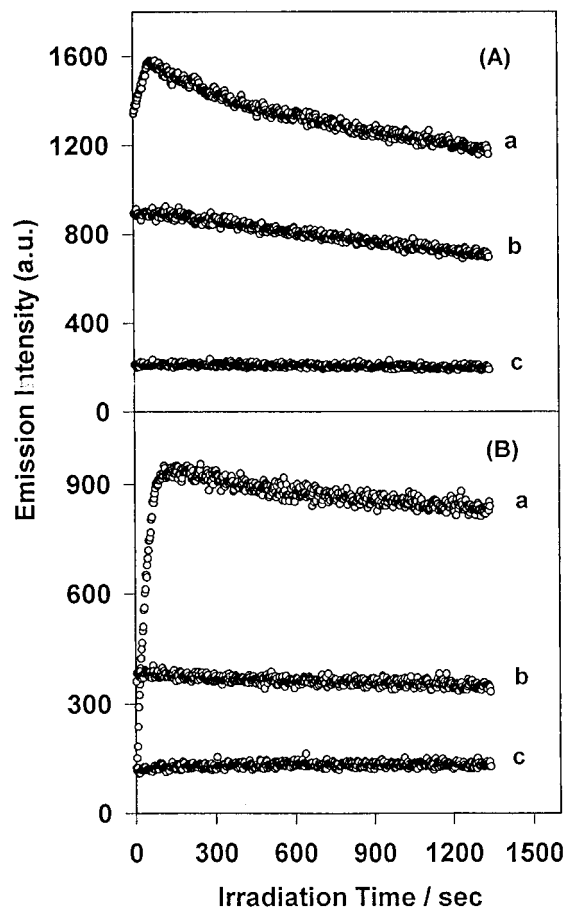

Figure 5. Irradiation effect on the emission of the polymer at different pressures: (A): At 450 nm (22 200 cm^{-1}); (a) 1 atm, (b) 5 kbar, and (c) 20 kbar. (B) At 560 nm (17 900 cm^{-1}), (a) 1 atm, (b) 6 kbar, and (c) 20 kbar.

and 550 nm). This is in the region where the radiation-induced emission is dominant. The relaxation is somewhat more rapid in the neat polymer, but both are considerably slower than for dissolved BP. In Figure 10 we compare the relaxation in PVBP−PS at 20 000 and 22 200 cm^{-1} (500 and 450 nm). At 500 nm (Figure 10A) the relaxation is essentially the same as that at 550 nm (Figure 9B). At 450 nm the relaxation is significantly faster. At this energy there is considerable delayed fluorescence as well as phosphorescence from the original molecule. The rise in intensity is only ~30% and while the data could be fit with a single exponential, it is possible that more than one relaxation is occurring. As for dissolved BP, at even a few kilobar pressure no relaxation was observed.

Discussion

Since we apparently observe both delayed fluorescence and triplet excimer emission as well as phosphorescence, we summarize very briefly the most directly relevant information in the literature on these topics. A number of experimentalists have observed delayed fluorescence in rigid solutions or polymers.[10−13] From our standpoint the essential feature is that, while the peak is centered at higher energy than the phosphorescence, the tail extends strongly under the phosphorescent peak so that, particularly if the delayed fluorescence is intense as in PVBS−PS, the changes in intensity with pressure of the two emissions are strongly coupled. A number of authors[10,13] indicate that the delayed fluorescence for BP occurs via back-feeding from T$_1$ to S$_1$ rather than via T$_2$ or by T$_1$ + T$_1$ annihilation, since the process is thermally activated. We assume that a significant fraction of the emission in the region
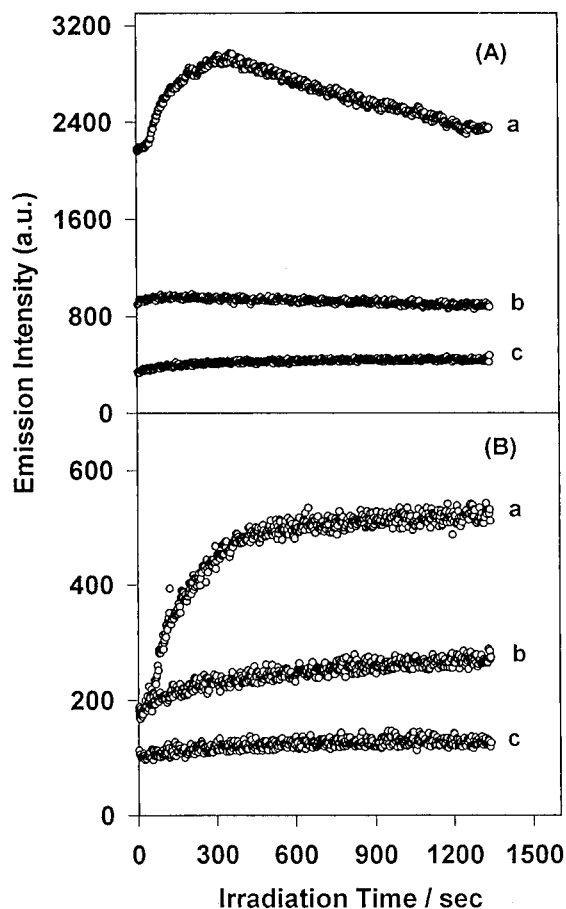
Figure 6. Irradiation effect on the emission of PVBS (10%) in PS at different pressures. (A) At 450 nm (22 200 cm^{-1}): (a) 1 atm, (b) 9 kbar, and (c) 30 kbar. (B) At 550 nm (18 200 cm^{-1}): (a) 1 atm, (b) 9 kbar, and (c) 29 kbar.

Figure 7. Irradiation effect on the emission spectrum of the polymer PVBS at different pressure: (A) 5 kbar, (○) before irradiation and (●) after irradiation; (B) 20 kbar, (○) before irradiation and (●) after irradiation.

550−560 nm (17 900−18 200 cm^{-1}) in PVBS (the neat polymer film) comes from a triplet excimer. Triplet excimers are very uncommon in liquids or even in low-temperature glasses. They are, however, less rare in polymers. They have been observed, e.g., in poly(vinylcarbazole) and in poly(vinylnapthalene).[14−18]

In an extensive set of experiments O'Connor et al.[19,20] studied fluorescence yields for copolymers of styrene with two aromatic molecules as a function of copolymer concentration and temperature. The most significant results were quenching of the styrene monomer and excimer emission by energy migration to the quenching molecule as well as Förster radiationless energy transfer. They found that the energy migration was temperature independent.

In the work presented here there is no direct fluorescence because of rapid intersystem crossing. The emission is from triplet monomer and, in the case of the neat polymer, the triplet excimer, as well as delayed fluorescence by back-donation from T_1 to S_1. For triplet states Förster energy transfer does not occur. These authors discuss the literature on energy migration, and their studies illustrate very well the effect of copolymer concentration on the migration and quenching of excitation. Since we present the effect of pressure at one copolymer concentration, there is no straightforward way to involve these considerations in our analysis.

The situation in the materials used in the current work is more complex than for BP dissolved in polymers[2,3,5] in that, besides the processes described in those papers, there exist the rate process from T_1 back to S_1 as well as the rate of excimer formation and possible decay to the monomer. In addition, there is the problem of strong overlap between the tail of the delayed
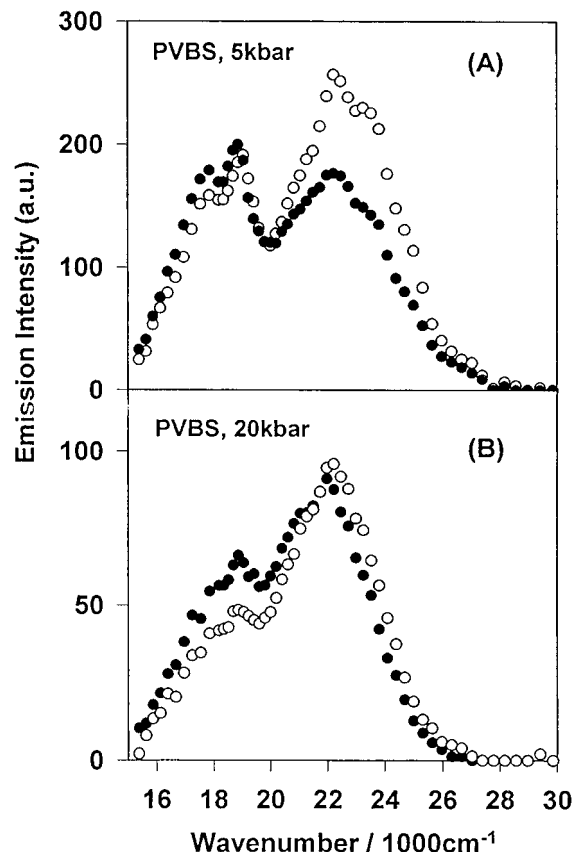
fluorescence and the monomer phosphorescence, of particular importance in PVBS−PS, and the overlap of the monomer and excimer emission, of considerable importance for PVBS.

Photophysical (Pure Pressure) Effects. The pure photophysical effects can be derived from Figures 3 and 4 and Table 1, keeping in mind that Table 1, derived from measurements of the spectra taking several minutes, must contain some radiation effects. Figure 11 illustrates these photophysical processes.

To simplify the discussion, we assume, in first order, that for the neat polymer the delayed fluorescence is sufficiently weak that changes with pressure and its presence under the phosphorescence can be ignored.

The most striking feature of the pressure effect in PVBS is the sharp rise in the intensity at 560 nm and the corresponding drop in the intensity at 450 nm in 2−3 kbar. The volume change for PS in this range is only $2^1/_2$−3%, and PVBS should not be markedly different. This is apparently sufficient to stabilize excimer formation at the expense of the monomer. The reduction in distance between BP entities on the chain or between chains is clearly insufficient to be important, but it may be that the relative motion of two BP elements is inhibited in a manner to enhance excimer formation or stability. Between 3 and 10 kbar neither band shows significant intensity change. At higher pressures the two bands both decrease in intensity. An increase in vibrational coupling with the matrix would increase the nonradiative rate for the monomer (and probably for the excimer). The equilibrium constant between monomer and excimer appears to have only modest pressure dependence after the first 5 kbar.

For the polymer dissolved in PS PVBS−PS a reasonable assumption is that excimer formation is negligible compared
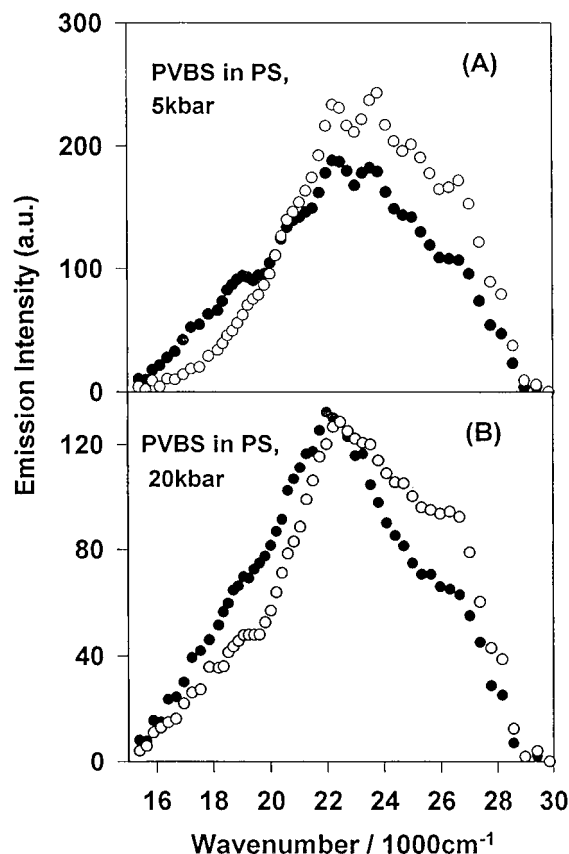
Luminescent Properties of PVBS—PS

J. Phys. Chem. B, Vol. 101, No. 21, 1997 **4223**

Figure 8. Irradiation effect on the emission spectrum of PVBS (10%) in PS at different pressure: (A) 5 kbar, (○) before irradiation and (●) after irradiation; (B) 20 kbar, (○) before irradiation and (●) after irradiation.

TABLE 2: Radiation Effects Ratio of Emission Intensity after/before 22 min Irradiation[a]

(A) From 25 min Irradiation Data

	A/B (390)	A/B (450)	A/B (500)	A/B (550)	A/B (560)
PVBS					
1 atm		0.89			7.6
6 kbar		0.74			0.96
20 kbar		0.95			1.27
PVBS—PS					
1 atm	0.59	1.1	2.21	2.94	
5 kbar		0.83		2.07	
9 kbar		0.88		1.53	
17 kbar	0.65				
30 kbar		1.07		1.27	

(B) From Spectra Taken before and after 25 min Irradiation

	A/B (390)	A/B (450)	A/B (550)
PVBS			
6 kbar	0.73	0.69	1.04
20 kbar	0.75	0.96	1.36
PVBS—PS			
5 kbar	0.62	0.78	1.89
20 kbar	0.68	1.02	1.52

[a] B = before irradiation; A = after 25 min irradiation; 390nm = 25 640 cm^{-1}, 450 nm = 22 200 cm^{-1}, 500 nm = 20 000 cm^{-1}; 550 nm = 18 200 cm^{-1}; 560 nm = 17 900 cm^{-1}.

with the emission from the monomer and the delayed fluorescence. At 22 200 cm^{-1} (450 nm) there is strong overlap between monomer emission and delayed fluorescence. However, at 20 000 cm^{-1} (500 nm) one should be observing essentially pure monomer emission. The intensity change with pressure, a modest rise, and then a slow decrease by a factor of about 2 from 7 to 30 kbar is very like that observed for BP dissolved in PVCl,[4] but both rise and drop are smaller here. At
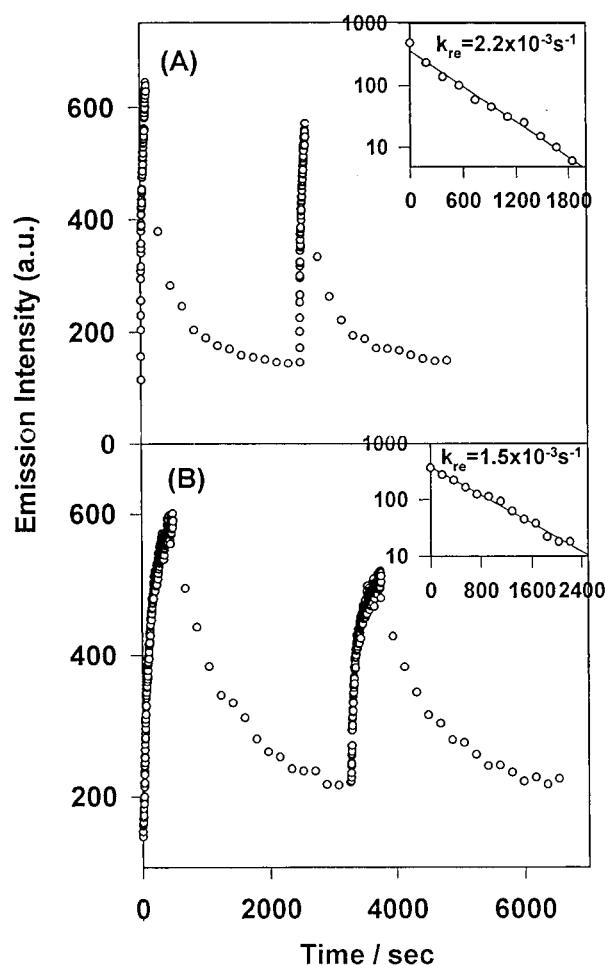

Figure 9. Reversibility of the emission of the polymer PVBS and PVBS (10%) in PS after irradiation at 1 atm. In the rising part of the curves the sample is under continued irradiation. In the descending part of the curves the sample is in the dark, except one second excitation for the measurement for each point. The insert includes the rate of relaxation taken from the first cycle: (A) PVBS, detected at 560 nm (17 900 cm^{-1}); (B) PVBS (10%) in PS, detected at 550 nm (18 200 cm^{-1}).

low pressure the dominant feature is an increase in the $\pi-\pi*$ content of the monomer triplet with resultant increase in the radiative rate and the luminescence efficiency. Above 5—7 kbar the increase in nonradiative rate due to stronger coupling to the matrix dominates.

The emission at 25 640 cm^{-1} (390 nm) represents delayed fluorescence. There is a sharp drop of almost 25% in the first 3 kbar and then a continuous decrease by factor of ~2 to 30 kbar. If one could correct the emission at 22 200 cm^{-1} (450 nm) for a significant fraction of delayed fluorescence, it would display a small maximum in the first 5 kbar essentially identical with that exhibited at 20 000 cm^{-1} (500 nm).

Between 5 and 30 kbar the intensity at 22 200 cm^{-1} (450 nm) drops by a factor of about 2—very similar to the behavior at 20 000 cm^{-1} (500 nm). The increase in nonradiative rate from the phosphorescence decreases the probability of delayed fluorescence, so that this emission drops as a result.

Photochemistry—Effects of Irradiation. The photochemical effects of irradiation are presented in Figure 5—10 and summarized in Table 2. We base much of our discussion on that table with occasional reference to the figures. The major feature, for both PVBS and PVBS—PS, is the large increase in intensity in the region of 18 000 cm^{-1} both absolutely and relative to the intensity at 22 200 cm^{-1} (450 nm). This is illustrated clearly in Table 2A,B and perhaps most dramatically in Figure 7A.

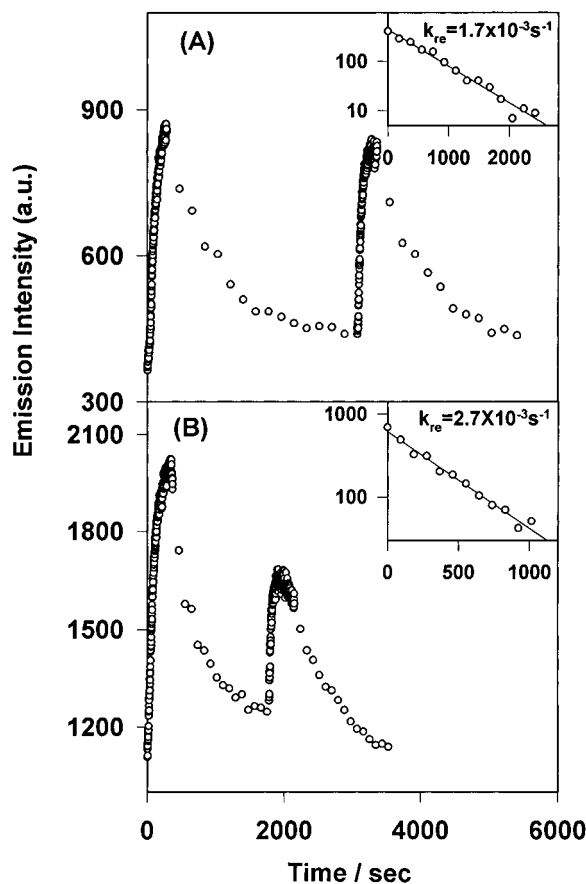**4224** *J. Phys. Chem. B, Vol. 101, No. 21, 1997*

Yang et al.

Figure 10. Reversibility of the emission of PVBS (10%) in PS after irradiation at 1 atm. In the rising part of the curves the sample is under continued irradiation. In the descending part of the curves the sample is in the dark, except one second excitation for the measurement for each point. The insert includes the rate of relaxation taken from the first cycle: (A) detected at 500 nm (20 000 cm^{-1}); (B) detected at 450 nm (22 200 cm^{-1}).
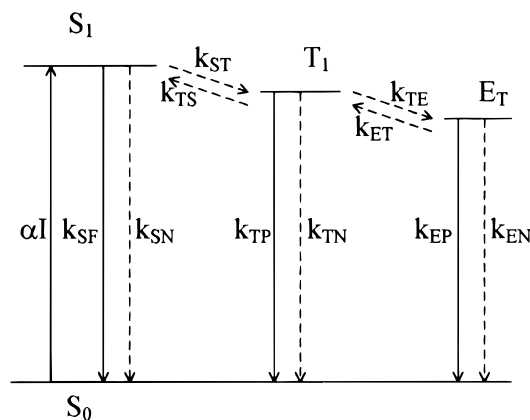

Figure 11. Photophysical processes in the polymer PVBS and PVBS (10%) in PS.

We attribute this to the creation of a new emitting product through hydrogen abstraction, a process observed with BP as well as other aromatic carbonyls dissolved in polymers. The new peak is some 4000 cm^{-1} lower in energy than the original phosphorescence. For BP dissolved in various polymers the irradiation-induced emission is essentially coincident with the original phosphorescence, while for 4,4′-dichlorobenzophenone the new peak is shifted some 1500−1800 cm^{-1} to the red.[5] In (dimethylamino)benzaldehyde where both fluorescence and phosphorescence is observed, radiation introduces a new fluorescence shifted ∼1500 cm^{-1} to higher energy and a new phosphorescence shifted ∼1500 cm^{-1} to lower energy.[5]

It is of interest that at 1 atm the radiation induces a greater increase in intensity in PVBS than in PVBS−PS. It is possible that this is due to a greater $\pi-\pi^*$ content in the radiation-induced PVBS emission. While the radiation-induced emission overlaps strongly the excimer emission, it occurs at the same location in PVBS−PS where there is little or no excimer formation. The radiation-induced emission decreases with increasing pressure, especially relative to the emission at 22 200 cm^{-1} (450 nm). This decrease is somewhat more rapid in PVBS than in PVBS−PS. Evidently compression inhibits geometrical changes associated with the reaction.

A second effect of radiation is to reduce the intensity of delayed florescence. This effect is especially evident for PVBS−PS where the original intensity at 25 000−26 000 cm^{-1} (390−400 nm) is much stronger at atmospheric pressure. A large part of this decrease in intensity is due to the formation of the new phosphorescence at 4000 cm^{-1} lower energy which reduces the amount of original phosphor available for $T_1 \rightarrow S_1$ back-conversion.

There is some evidence for the photoconversion to a nonemitting species via T_2 which was evident for aromatic carbonyls dissolved in polymers, but it is a lesser factor and masked by the complexity of other phenomena.

Conclusions

The luminescence from a polymer based on polystyrene but with approximately one in seven styrenes replaced by benzophenone was studied as a function of pressure both as a neat polymer (PVBS) and dissolved in 10% concentration in polystyrene PVBS−PS. In addition to the phosphorescence typical for dissolved BP (at 22 200 cm^{-1}) the PVBS exhibited an emission at ∼18 000 cm^{-1} attributed to an excimer and a weaker emission at ∼25 000−26 000 cm^{-1} attributed to delayed fluorescence. PVBP−PS exhibited little if any excimer emission but strong delayed fluorescence. The photophysical effects of pressure for PVBS involved a rapid increase in intensity at the excimer emission in 2−3 kbar followed by a decrease in both excimer and monomer emission intensity. For PVBS−PS the phosphorescence increased modestly at low pressure and then decreased, much like the behavior of BP dissolved in PVCl, but the effects are smaller in magnitude.

A major effect of radiation for both materials was the introduction of a new emission about 4000 cm^{-1} lower in energy than the original phosphorescence. This is attributed to the formation of a new emitting product by hydrogen abstraction from the matrix and subsequent reaction. In addition, there was a clear decrease in the amount of delayed fluorescence with increasing pressure attributed to the creation of the new phosphorescence at lower energy which reduces the amount of original phosphor available for $T_1 \rightarrow S_1$ back-conversion.

References and Notes

(1) Dreger, Z. A.; Lang, J. M.: Drickamer, H. G. *Chem. Phys. Lett.* **1995**, *232*, 351.

(2) Dreger, Z. A.; Lang, J. M.; Drickamer, H. G. *J. Phys. Chem.* **1996**, *100*, 4637.

(3) Dreger, Z. A.; Lang, J. M.; Drickamer, H. G. *J. Phys. Chem.* **1996**, *100*, 4646.

(4) Dreger, Z. A.; Drickamer, H. G. *J. Phys. Chem.*, in press.

(5) Dreger, Z. A.; Drickamer, H. G. *J. Phys. Chem.,* in press.

(6) David, C.; Demarteau, W.; Geuskens, G. *Polymer* **1969**, *10*, 21.

(7) Piermarini, G. J.; Block, S. *Rev. Sci. Instrum.* **1975**, *46*, 973.

(8) Dreger, Z. A.; Drickamer, H. G. *Chem. Phys. Lett.* **1991**, *179*, 199.

(9) Dreger, Z. A.; Lang, J. M.; Drickamer, H. G. *Chem. Phys. Lett.* **1991**, *185*, 184.

(10) Sun, Y.-P.; Sears, D. F., Jr.; Saltiel, J. *J. Am. Chem. Soc.* **1989**, *111*, 706.

(11) Saltiel, J.; Curtis, H. C.; Metts, L.; Miley, J. W.; Winterle, J.; Wrighton, M. *J. Am. Chem. Soc.* **1970**, *92*, 410.

(12) Brown, R. E.; Singer, L. A.; Parks, J. H. *Chem. Phys. Lett.* **1972**, *14*, 193.

(13) Jones, P. F.; Calloway, A. R. *Chem. Phys. Lett.* **1971**, *10*, 438.

(14) Webber, S. C. In *Polymer Photophysics*, Phillips, D., Ed.; Chapman and Hall: London, 1985, p 49.

(15) Burkhart, R. D.; Caldwell, N. J. In *Photophysics of Polymers*; Hoyle, C. E., Torkelson, J. M., Eds.; ACS Symposium Series 358; American Chemical Society: Washington, DC, 1987; p 246.

(16) Klopffer, W.; Fischer, D. *J. Polym. Sci., Part C* **1973**, *40*, 43.

(17) Burkhart, R. D.; Aviles, R. G.; Magrini, K. *Macromolecules* **1981**, *14*, 91.

(18) Burkhart, R. D.; Lee, O.; Boileau, S.; Boivin, S. *Macromolecules* **1985**, *18*, 1277.

(19) O'Conner, D. B.; Scott, G. W.; Coulter, D. R.; Yavrouian, A. *Macromolecules* **1991**, *24*, 2355.

(20) O'Conner, D. B.; Scott, G. W.; Coulter, D. R.; Yavrouian, A. *J. Phys. Chem.* **1991**, *95*, 10252 and references therein.