Emission and absorption studies on poly(methyl vinyl ketone): evidence of ground state complex formation with alkyl amines

S. W. Beavan and W. Schnabel
Hahn-Meitner-Institut für Kernforschung Berlin GmbH, Bereich Strahlenchemie, Glienicker Str. 100, D-1000 Berlin 39, W. Germany

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INTRODUCTION

It has recently been reported that the fluorescence of low molecular weight aliphatic ketones such as 2-pentanone is quenched by aliphatic amines [diethylamine(DEA) and triethylamine (TEA)][1–3]. From the results obtained it was inferred that $^1n\pi^*$ state quenching occurred by charge transfer stabilized exciplex formation.

As will be shown in this paper, the fluorescence spectrum of a polymeric aliphatic ketone, poly(methyl vinyl ketone) (PMVK), undergoes significant alterations by the addition of low molecular weight aliphatic amines to its solutions. It could be concluded that these alterations are due to ground state complex formation of PMVK and DEA or TEA, respectively.

EXPERIMENTAL

A Perkin–Elmer MPF 4 spectrofluorimeter was used for the emission measurements and a Zeiss double beam spectrometer was used for the absorption measurements.

Methylene chloride, cyclohexane, ethyl acetate and *p*-dioxane (all Merck, spectroscopy grade) were used as delivered. Acetone (Merck, spectroscopy grade) was distilled via a splitting tube column. Both diethylamine and triethylamine were stored over NaOH pellets for 24 h prior to refluxing for 6 h over sodium wire. Finally they were fractionally distilled. Two PMVK samples ($\bar{M}_w$ = 2.2×10^6 and 8.6×10^5) were used. Preparation and characterization have been described before[6].

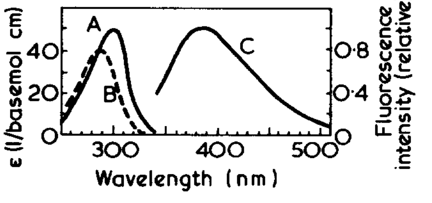

Figure 1 U.v. absorption (— — —) and uncorrected fluorescence emission and excitation spectra (———) of PMVK in methylene chloride solution (1.06×10^{-2} base mol/l), at room temperature. Emission spectrum obtained with λ_{exc} = 313 nm, excitation spectrum obtained with λ_{record} = 390 nm. A, Fluorescence excitation; B, absorption; C, fluorescence emission

RESULTS

Figure 1 shows absorption and emission spectra of PMVK recorded in methylene chloride solution at 25°C. The same spectra were obtained in the absence and presence of air. The spectra are in good agreement with those presented by Sommersall and Guillet[4] who used ethyl acetate as solvent. Using methylene chloride, ethyl acetate and *p*-dioxane as solvents, we have found that the absorption and emission spectra are only weakly dependent on the solvent. The fluorescence quantum yield $\phi(F)$ of PMVK in CH_2Cl_2 was found to be 7.2×10^{-4} using acetone in cyclohexane as standard [$\phi(F)$ = 9.9×10^{-4} at 25°C].

Figure 2 shows the emission spectra obtained with PMVK solutions (CH_2Cl_2) at various amine concentrations. It can be seen that for both the PMVK/DEA and the PMVK/TEA systems the emission intensity at wavelengths less than about 440 nm decreases with increasing amine concentration. Above 440 nm, on the other hand, the emission intensity increases with increasing amine concentration. With CH_2Cl_2 solutions containing DEA or TEA up to 2 M no long wavelength emission was observed. Thus the possibility that the emission observed with PMVK is due to an impurity contained in the amine can be excluded. Since similar results were obtained with dioxane solutions and with CH_2Cl_2 solutions the possibility that the new emission is due to CH_2Cl_2–amine interaction may also be excluded.

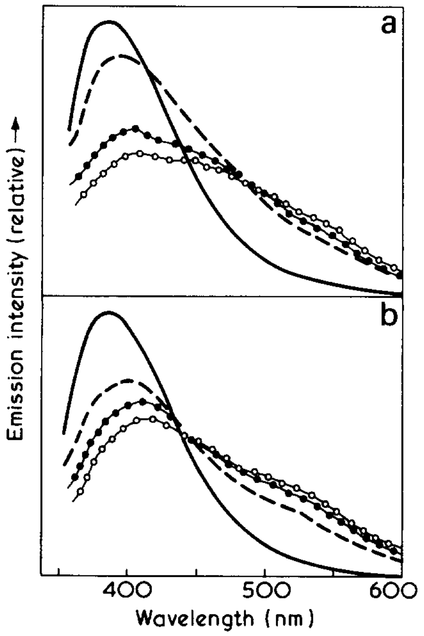

Figure 2 Emission spectra of PMVK in methylene chloride solution (1.85×10^{-2} base mol/l) at amine concentrations at room temperature and λ_{exc} = 313 nm. (a) TEA: ——, 0; — — —, 0.78 mol/l; ●, 1.8 mol/l; ○, 7.3 mol/l. (b) DEA: ——, 0; — — —, 0.39 mol/l; ●, 1.7 mol/l; ○, 7.1 mol/l

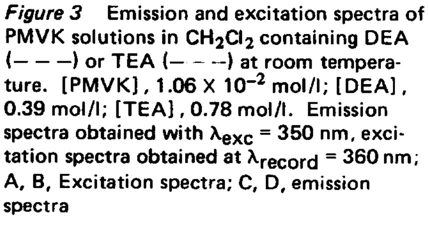

Figure 3 Emission and excitation spectra of PMVK solutions in CH_2Cl_2 containing DEA (— — —) or TEA (— - —) at room temperature. [PMVK], 1.06×10^{-2} mol/l; [DEA], 0.39 mol/l; [TEA], 0.78 mol/l. Emission spectra obtained with λ_{exc} = 350 nm, excitation spectra obtained at λ_{record} = 360 nm; A, B, Excitation spectra; C, D, emission spectra

Figure 3 shows excitation and emission spectra obtained in presence of DEA and TEA, respectively. The emission spectra are corrected for the emission of pure PMVK. It is seen that in the presence of amine the excitation spectra are red-shifted (maxima at ~400 nm) relative to the excitation spectrum obtained in the absence of amine (maximum at 280 nm, see *Figure 1*). The spectral distribution of the emission spectra was found to be inde-

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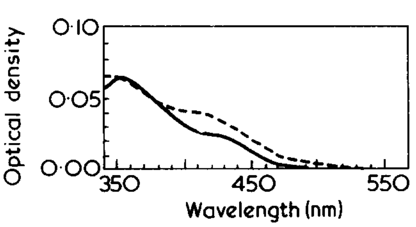

Figure 4 Absorption spectra of methylene chloride solutions of PMVK (1.86×10^{-2} base mol/l) containing TEA: (———), 2.40×10^{-2}M and DEA (– – –), 3.25×10^{-2}M at room temperature. Path length 10 cm. Reference: 1.86×10^{-2} base mol/l PMVK/methylene chloride solution

pendent of the excitation wavelength and the amine concentration. Absorption spectra obtained in the presence of DEA or TEA are shown in *Figure 4*. The amine/CH_2Cl_2 charge transfer absorption at the PMVK concentrations used is negligible at $\lambda > 300$ nm. Clearly, there is an absorption above 340 nm where PMVK does not absorb. Oxygen did not influence the spectra shown in *Figure 4*.

DISCUSSION

The results obtained strongly suggest that PMVK forms a ground state complex with the amines:

$$\mathrm{PMVK} + \mathrm{A} \rightleftharpoons (\mathrm{PMVK} \cdots\cdots \mathrm{A}) \quad (1)$$

This suggestion was corroborated by the observed variations of the emission intensity and the extent of the absorption with variation of either the PMVK or the amine concentration. Based on the assumption that the absorption above 340 nm and the emission above 550 nm are proportional to the complex concentration, the following conclusions can be made. In the presence of an excess of PMVK the complex concentration increased linearly with amine concentration. As the concentration of the amine approached the total concentration of PMVK the complex concentration levelled off. In the presence of excess amine the complex concentration increased linearly with increasing PMVK concentration. This behaviour is typical for an interaction resulting in a 1:1 equilibrium complex.

It may be emphasized that for low molecular weight aliphatic ketones, containing only one carbonyl group, complex formation with alkyl amines could not be observed[3]. It appears possible, therefore, that neighbouring carbonyl groups in the main chain of the polymer are involved in the ground state interaction of PMVK and alkyl amines.

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