G. Weiser
H. Seki

Charge Transfer Complex Formation of Trinitrofluorenone with Polyvinylcarbazole and Ethylcarbazole

Abstract: The molar absorption constants of the charge-transfer complexes of PVCz:TNF and of ethylcarbazole:TNF and the respective equilibrium constants for the formation of these complexes in a tetrahydrofuran solution have been determined by absorption measurements. Both materials exhibit two charge-transfer absorption bands. It is shown that these two bands correspond to two transitions of only one charge-transfer complex rather than to two complexes with different geometrical configurations of donor and acceptor molecules. For the PVCz:TNF complex the equilibrium constant is determined as $K = 0.5$ l/mole, which is much smaller than the value $K = 3.05$ l/mole found for the complex of ethylcarbazole and TNF.

Introduction

Poly-N-vinylcarbazole (PVCz) and 2,4,7-trinitro-9-fluorenone (TNF) form a charge-transfer complex with an absorption spectrum extended over the entire visible region [1]. Solid films of this material exhibit efficient photoconductivity [2]. Mobility measurements indicate that the amount of TNF plays an important role in the electron mobility of the mixture [3] but it is still unknown how much of the TNF in these films is complexed and how much remains free. As a first step to answer this question the equilibrium constant for the formation of the charge-transfer complex in solution (tetrahydrofuran) and the molar absorption constant were determined. The results are compared with measurements on the charge-transfer complex of TNF with N-ethylcarbazole (EtCz), which is essentially a monomer form of PVCz.

Measurement technique

• *Samples and measurements*

Highly purified PVCz, TNF and EtCz were dissolved in tetrahydrofuran (THF) in the desired concentrations. The absorption spectra of these solutions were measured in a double-beam recording spectrometer (Cary Model 14). The tail of the absorption characteristic of the TNF molecules was subtracted from the absorption of the mixture.

The usual way to determine the equilibrium constant K and the molar absorption constant α_0 of a charge transfer complex uses a Benedisi-Hildebrand plot [4] which requires a large excess of one component and deals with very small concentrations of complexed molecules. This condition is very different from the situation in solid photoconductive films, where the concentration of the two components is of the same order of magnitude and the concentration of the complexed molecules is high. We therefore chose to determine the equilibrium constant from solutions involving higher relative concentrations of the components, mixed in a ratio similar to that in solid films. Most of the measurements were performed on solutions with a molar ratio of 1:0.2 of PVCz monomer units to TNF. The concentration of PVCz varied between 0.03 and 0.25 mole/l. Samples with higher content of TNF gave the same results. The measurements on the charge transfer complex of ethylcarbazole and TNF were performed in the same way with the same concentrations of the solution as used in the experiments on PVCz:TNF.

• *Analysis*

The equilibrium constant K and the molar absorption constant α_0 of the charge transfer complexes were obtained by using a modified Benedisi-Hildebrand plot. If the formation of the complex follows the relation

$$\mathrm{PVCz} + \mathrm{TNF} \rightleftarrows \mathrm{PVCz{:}TNF} \tag{1}$$

the equilibrium constant K is given by the actual concentrations of the different components in this reaction:

$$K = \frac{[\text{PVCz:TNF}]}{[\text{PVCz}]\,[\text{TNF}]}. \tag{2}$$

Equation (2) is already an approximation which neglects the possibility that the equilibrium itself depends slightly on the concentration of the solution [5]. With c_k defined as the concentration of the complex [PVCz: TNF] and c_p, c_t the respective total concentrations of PVCz and TNF (both complexed and uncomplexed), one gets the equations

$$c_k = K(c_p - c_k)\ (c_t - c_k) \tag{3}$$

and

$$c_k^{\ 2} - c_k\left(\frac{1}{K} + c_p + c_t\right) + c_p c_t = 0\,. \tag{4}$$

In our experiments $c_p c_t$ varied between 2×10^{-4} and 10^{-2} $(\text{mole/l})^2$. If K is of the order of 1 l/mole or smaller then c_k varies approximately as $c_p c_t$ and $c_k^{\ 2}$ becomes negligible compared with the other terms in Eq. (4) leading to

$$-c_p c_t = c_k\left(\frac{1}{K} + c_p + c_t\right). \tag{5}$$

Assuming that the molar absorption constant α_0 of the charge-transfer complex does not depend on the concentration of the solution, the absorption of the solution is directly proportional to the concentration of the complexed molecules

$$\alpha = \alpha_0 c_k\,. \tag{6}$$

Combining Eqs. (5) and (6) finally leads to the relation

$$\frac{c_p c_t}{\alpha} = \frac{1}{\alpha_0}\,(c_p + c_t) + \frac{1}{K\alpha_0}, \tag{7}$$

which was used in the evaluation of the optical data.

Experimental results

• *PVCz:TNF Charge-transfer complex*

The absorption spectrum of the charge-transfer complex of PVCz and TNF dissolved in THF is shown in Fig. 1. The full curves represent the absorption of two solutions of different concentrations, the ratio of monomer units PVCz and TNF being 1:0.2. The absorption of the complex increases approximately in proportion to $c_p c_t$ which, according to Eq. (3), indicates a small equilibrium constant. The strong increase of the absorption above 2.8 eV is due to the onset of the absorption of the TNF. The dashed curves in Fig. 1 show the absorption spectrum of the same samples six days later. The solution with the smaller concentration shows a strong increase of the absorption. With rising concentration of the solution this aging effect becomes smaller and is not observed on samples with $c_p > 0.1$ mole/l and $c_t > 0.02$ mole/l. Since the same aging effect is found for solutions of pure TNF and THF it must be caused by some reaction of the TNF molecules in the solvent and is not directly relevant to the formation of the charge-transfer complex. In order to avoid the effects of this additional absorption only measurements on fresh solutions with concentrations of $c_p > 0.07$ mole/l and $c_t > 0.014$ mole/l were taken into account.

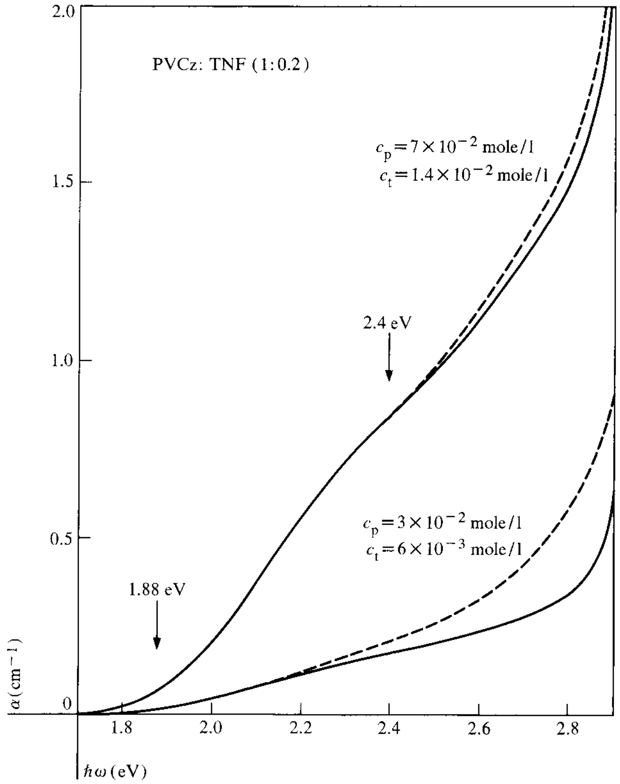

Figure 1 Absorption spectra of two solutions of PVCz:TNF in tetrahydrofuran (THF). The full curves represent the spectra of fresh solutions, the dashed curves give the spectra of the same samples but six days later.

Electroabsorption measurements on solid films of 1:1 PVCz:TNF have shown that the charge-transfer absorption band consists of two bands with absorption edges at 1.88 eV and 2.4 eV [6], marked by the arrows in Fig. 1. It was not clear whether these absorption bands corresponded to two transitions of one charge-transfer complex or to the excitation of two different charge-transfer complexes with different steric configurations of acceptor and donor molecules. In the latter case the probability of forming a charge-transfer complex should be different for the two complexes, leading to a different increase of the two absorption bands with increasing concentration of the solution and resulting in an alteration of the shape of the charge-transfer absorption spectrum.

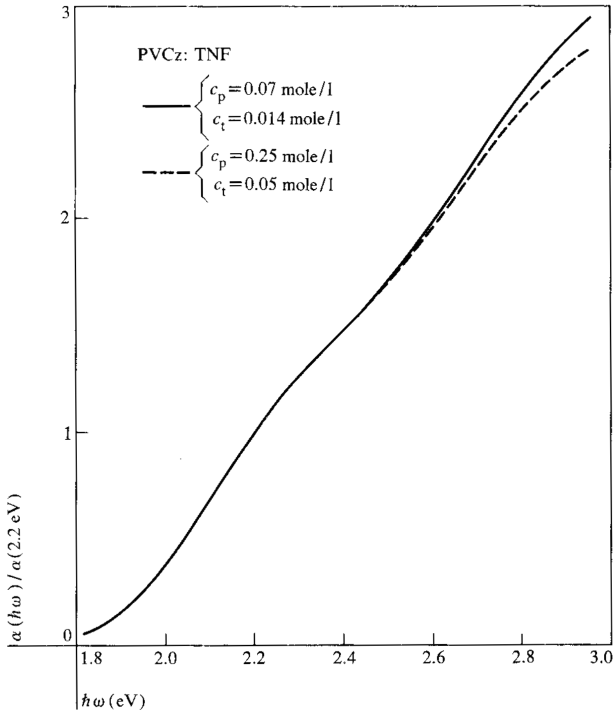

Figure 2 Normalized absorption spectra of two solutions with different concentration of PVCz and TNF. $r(\hbar\omega) = \alpha(\hbar\omega)/\alpha(2.2\ \text{eV})$.

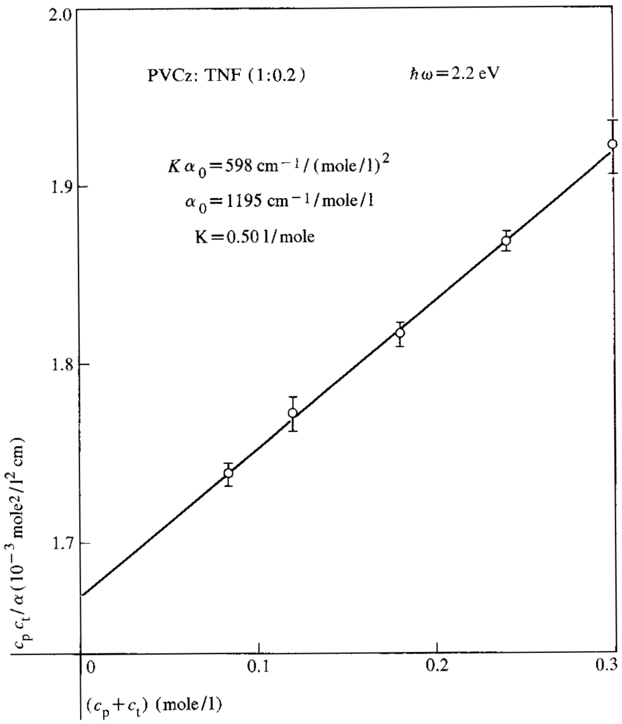

Figure 3 Determination of the equilibrium constant for the formation of the charge-transfer complex of PVCz:TNF. According to Eq. (7) the slope of the straight line gives the reciprocal value of the molar absorption constant. The intersection with the ordinate gives the value of $1/K\alpha_0$.

The net change of shape of the absorption spectrum can be detected by normalization of the absorption curves of different solutions. Figure 2 shows $r(\hbar\omega) = \alpha(\hbar\omega/\alpha(2.2\text{eV})$, the absorption curves of two solutions with different concentration of PVCz and TNF normalized to $\alpha(2.2\ \text{eV}) = 1$. The absorption tail of TNF at energies above 2.6 eV was previously subtracted. The absolute value of the absorption of both solutions differs by a factor greater than 10 but the normalized curves match almost perfectly at energies below 2.5 eV. The small deviation at higher energy appears too small to be explained by a different equilibrium constant K in this region. This deviation is more likely caused by a slight change of the molar absorption constant α_0 due to the stronger interaction of the complexed molecules at higher concentration. Obviously this alteration of the molar absorption can be different for the two transitions, resulting in a small deviation of the normalized curves. The rise of both absorption bands of the charge-transfer absorption region with increasing concentration of PVCz and TNF can be described by one equilibrium constant K, which strongly favors the explanation of these bands by two transitions of a single charge-transfer complex.

The equilibrium constant K was determined using the absorption spectrum between 1.9 eV and 2.4 eV where the normalized absorption curves of the different solutions coincided. This was done by using the normalized absorption curve $r(\hbar\omega)$ in Fig. 2 which is proportional to $\alpha_0(\hbar\omega)$ to reduce all the absorption data at different energies to the absorption corresponding to 2.2 eV (which was chosen arbitrarily), i.e., $\alpha(\hbar\omega,c_p,c_t)/r(\hbar\omega)$. Figure 3 shows the result of this procedure for determining K according to Eq. (7) where $r(\hbar\omega)c_pc_t/\alpha(\hbar\omega,c_p,c_t)$ is plotted against $c_p + c_t$. The points correspond to the averaged absorption constants at 2.2 eV and fit a straight line fairly well. The bars cover the range over which the values $\alpha(\hbar\omega,c_p,c_t)/r(\hbar\omega)$ for various $\hbar\omega$ scatter. This procedure is essentially equivalent to using the area below the absorption curve for the energy range involved as a measure of the absorption strength rather than the absorption constant at one particular energy. The molar absorption constant α_0 at 2.2 eV is obtained from the slope of the straight line. This value $\alpha_0 = 1195\ \text{cm}^{-1}$ mole/l is less accurate than the value $K\alpha_0 = 598\ \text{cm}^{-1}/(\text{mole/l})^2$ given by the intersection of the straight line and the ordinate axis. Combining both results leads to the equilibrium constant $K = 0.50$ l/mole.

Figure 4 shows another plot of the absorption data based on Eq. (3). In the case of a small equilibrium constant K and of low concentrations ($c_k \ll c_p,c_t$) a plot of

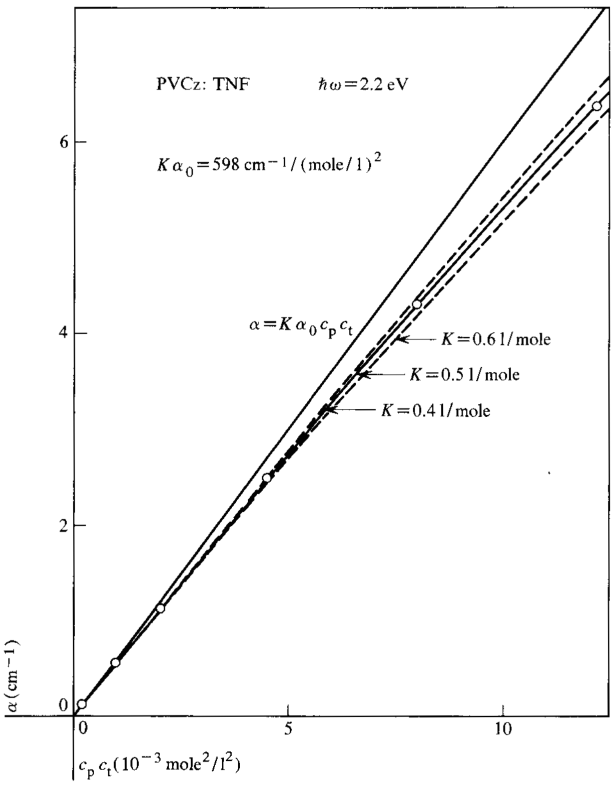

Figure 4 Plot of the absorption constant α of the PVCz:TNF complex versus $c_p c_t$ according to Eq. (3). The points represent experimental values, the curves are calculated for different values of K but with the same value $K\alpha_0 = 598$ cm^{-1}/(mole/l)^2 taken from Fig. 3.

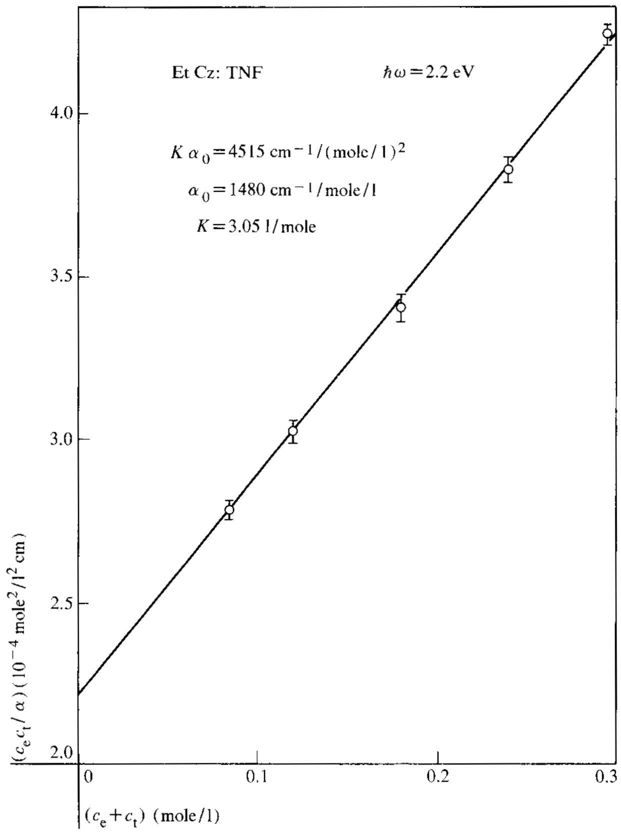

Figure 5 Determination of the equilibrium constant for the formation of the charge-transfer complex of N-ethylcarbazole and TNF according to Eq. (7).

the absorption constant α of the charge-transfer complex versus $c_p c_t$ gives a straight line with the slope $K\alpha_0$. The larger the value of the equilibrium constant K, the more the actual value of the absorption constant deviates from the straight line. Figure 4 shows three calculated curves with $K\alpha_0 = 598$ cm^{-1}/(mole/l)^2 and different values of K. The experimental points fit the curve for $K = 0.5$ l/mole very well. This method, however, is suitable for the determination of K only if an accurate value of $K\alpha_0$ already exists.

• *N-ethylcarbazole:TNF charge-transfer complex*

The absorption spectrum of the charge-transfer complex of N-ethylcarbazole (EtCz) and TNF looks very similar to that of the PVCz:TNF complex. The spectrum is extended over the same energy range and also exhibits two absorption bands. The main difference is that at the same concentration of donor and acceptor molecules in the solution, the absorption of the EtCz:TNF solution is much stronger than the absorption of the PVCz:TNF solution. This result is surprising in view of the similarity of PVCz and EtCz, which is essentially a monomer unit of the PVCz. The stronger absorption of the EtCz:TNF solution could be caused by a higher molar absorption constant or, more likely, by a larger equilibrium constant for the formation of the complex. In the range of both absorption bands of the complex between 1.8 eV and 2.8 eV the increase of the absorption with rising concentration of the solution is described by one equilibrium constant. The chemical equilibrium constant K and the molar absorption constant α_0 were initially determined by the same method as used previously for the PVCz:TNF complex.

Figure 5 shows an evaluation of the absorption data according to Eq. (7). The points represent averaged values as in Fig. 3, where the bars give the range in which the unaveraged values scatter. The molar absorption constant α_0 is determined from the slope of the straight line and is, at 2.2 eV, only slightly higher than the value found for the PVCz:TNF complex. The value of the chemical equilibrium constant K, which is determined as 3.05 l/mole, is much larger than the value obtained for the PVCz:TNF complex. At this value the c_K^2 term is no longer completely negligible in Eq. (4), but corrections can be made by an iterative procedure. This led to a value of $K = 3.29$ and $\alpha_0 = 1380$. The higher K value indicates

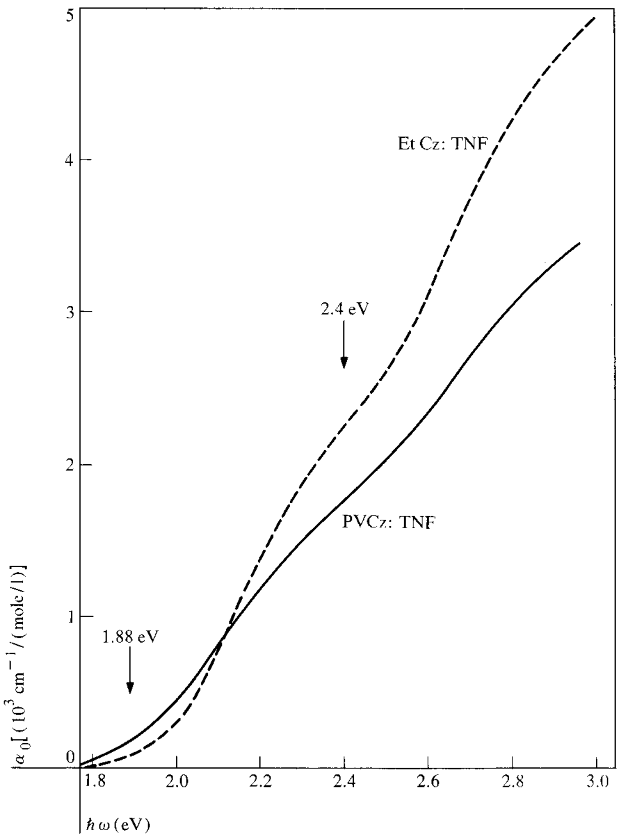

Figure 6 Spectral dependence of the molar absorption constant of the charge-transfer complex of PVCz:TNF (solid curve) and of the charge transfer complex of N-ethylcarbazole and TNF (dashed curve). The arrows mark the absorption edges of the two charge-transfer absorption bands as found by electroabsorption measurements on solid films of 1:1 PVCz:TNF [5].

that in the case of the EtCz:TNF complex the equilibrium between formation and dissociation of the complex is shifted in favor of formation. It is reasonable to attribute this difference to the steric hindrance which occurs in the case of the polymer.

- *Molar absorption constant*

With the knowledge of the equilibrium constant, and therefore the density of complexes in a solution, it is possible to determine the molar absorption constant from the absorption data. The full curve in Fig. 6 shows the energy dependence of the absorption constant α_0 of the charge-transfer complex of PVCz:TNF, derived from the value $\alpha_0(2.2\text{ eV}) = 1195\text{ cm}^{-1}$/mole/l from Fig. 3 and from the normalized absorption curve $r(\hbar\omega)$ in Fig. 2. The dashed line shows the spectrum of the charge-transfer complex of the ethylcarbazole and TNF, derived from the data in Fig. 5. The arrows indicate the two absorption edges as found by electroabsorption measurements on 1:1 PVCz:TNF films [6]. Both absorption spectra look similar but the absorption of the EtCz:TNF complex is somewhat higher and shows a sharper absorption edge. The two absorption bands of the PVCz:TNF complex are broader, which could be due to the fact that the carbazole groups are less movable on the polymer chain and therefore restrained in the formation of the complex.

Conclusions

The molar absorption constant α_0 of the charge-transfer complex of PVCz and TNF dissolved in tetrahydrofuran and its spectral dependence between 1.8 eV and 2.9 eV have been determined. The molar absorption changes slightly at higher concentration, probably because of the increasing interaction of the complexed molecules. The broad absorption band of the complex consists of two bands which overlap each other. By comparing the normalized absorption curves of solutions with different concentration, it was shown that the increase of the absorption with rising concentration of PVCz and TNF is described by only one equilibrium constant $K = 0.5$ l/mole. It is therefore very unlikely that the two absorption bands correspond to two charge-transfer complexes with different geometrical configurations of donor and acceptor molecules. It is much more reasonable to interpret these two absorption bands by transitions between different states of only one charge-transfer complex. This conclusion is supported by the comparison of the results on the PVCz:TNF complex with the very similar results on an ethylcarbazole:TNF complex. The increase of the absorption of the two charge-transfer absorption bands with rising concentration of the solution can also be described in this case by only one equilibrium constant which, however, has a higher value.

Further insight into the source of the two bands will depend on the knowledge of the energy-level structure of the complexes. At present even the geometry of the complex is unknown, let alone the energy levels of the complex. However the similarity of the frequency dependence of the molar absorption constant for PVCz:TNF and EtCz:TNF complex does suggest that the structure of the two complexes must be essentially similar. This would rule out structures which cannot be formed in the case of polymers. It is interesting that comparison between PVCz and EtCz of both the equilibrium constant K and the molar absorption constant spectra $\alpha_0(\hbar\omega)$ indicate complex formation appears more favored if the carbazol groups are not connected to a polymer chain. The value of $K = 1.52$ l/mole reported for N-isopropylcarbazol and TNF [7] is intermediate to the two cases discussed here and is consistent with this picture.

Finally it should be commented that the lower value of the equilibrium constant of 0.5 found in this study as compared to the value of 1.31 reported earlier [2] is due to more careful measurement and analysis. A study of the absorption data for the solid films of PVCz/TNF indicate an even lower "effective equilibrium constant", which is reasonable since the formation of the complex is not likely to reach equilibrium as the film dries [8].

Acknowledgments

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Dr. Seki is located at the IBM San Jose Research Laboratory, San Jose, California 95114. Dr. Weiser was engaged in post-doctoral work at the San Jose laboratory. He is now at the Physics Institute, University of Marburg, Marburg, Germany.