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Quantitative Evaluation of Polymeric Photosensitizers

1. Determination of Stern-Volmer Constants in Poly-*p*-(Vinyl-Acetophenone)- and Poly-*p*-(Vinyl-Benzophenone)-Stilbene Systems

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Summary

The energy transfer ability of free and polymer-bound acetophenone and benzophenone has been studied. The polymeric sensitizers were prepared by acetylation or benzoylation of atactic polystyrene ($\overline{M}n$=67.000). Trans-cis isomerization of stilbene, monitored by UV-spectrophotometry, has enabled the energy transfer process to be probed. The values of the Stern-Volmer constants, determined by following this technique, indicate that the energy transfer efficiency of both ketones is higher when they are in free state than when they are polymer-bound.

Introduction

The potential use of polymer-bound photosensitizers in photochemical synthesis and in chemical-based solar energy storage systems has promoted the study and development of these promising polymers (HAUTALA and LITTLE, 1980; NECKERS, 1978). In this paper we will describe our preliminary results concerning the use as photosensitizers of two keto-ring substituted polystyrenes: poly-p-(vinylacetophenone) and poly-p-(vinylbenzophenone).

Initially, we have focused our attention on the setting up of a technique directed to evaluate the energy transfer ability of this type of photosensitizers. Subsequently, we have applied it to compare the performances of these polymers with the monomeric models, acetophenone and benzophenone. A polymeric sensitizer in which the excitation energy can migrate up and down the chain and whose mobility differs appreciably from that of the monomer, is expected to transfer energy with a different efficiency. However, it has been reported in the literature that no significant difference was found between poly(vinylphenyl-ketone) and its monomeric counterpart, acetophenone, when used as cis-trans isomerization photosensitizers (MOSER and CASSIDY, 1964; IRIE et al.,1975). A similar conclusion arises from work done on poly-p(vinylbenzophenone) (SEARLE et al.,1967). Nevertheless, we consider that the quantitative evaluation of photosensitizers requires an experimental dispositive carefully designed to bring out small differences among them. Therefore, we thought it would be noteworthy to reinvestigate those findings with our technique. It is necessary to bear in mind that the quantitative evaluation of polymeric photosensitizers should constitute an essential guide to its rational preparation (MARTINEZ-UTRILLA and SASTRE, 1982).

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Stilbene has been chosen as the acceptor molecule to probe the energy transfer process. The use of this acceptor presents a great deal of advantages. Its ability to accept electronic energy from triplets of aromatic ketones is well documented (HAMMOND et al., 1964; SALTIEL et al., 1975) and, on the other hand, the possibility of monitoring the trans-cis isomerization by UV-spectrophotometry facilitates in a great measure the practical execution of a kinetic study.

Stern-Volmer constants, k_{SV} = kt/kd, (k_d = deactivation rate constant, sec^{-1}; k_t = energy transfer rate constant, M^{-1} sec^{-1}) are calculated from expression (1), where C_0 is the total concentration of stilbene (cis- plus trans-), and k_a is deduced from the integrated kinetic equation (2):

$$k_{SV} = \frac{k_a}{1 - k_a C_0} \quad (1) \qquad\qquad \ln \frac{1 - \phi_{CT}}{Y - \phi_{CT}} = I_a k_a t \quad (2)$$

In this equation, I_a is the intensity of absorbed light, einsteins sec^{-1} l^{-1}, "t" the irradiation time, sec, "Y" the ratio between the trans-stilbene (at time "t") and the total concentration C_0 and, finally, ϕ_{CT} is the quantum yield for the triplet stilbene cis → trans conversion.

In deriving formula (1) and (2), the following simplified scheme for the photosensitized stilbene isomerization has been taken into account:

$$(PPS) + h\nu \xrightarrow{I_a} {}^3(PPS)^* \qquad\qquad {}^3(PPS)^* \xrightarrow{k_d} (PPS)$$

$${}^3(PPS)^* + t\text{-}St \xrightarrow{k_t} (PPS) + {}^3St^* \qquad\qquad {}^3St^* \xrightarrow{k_3} t\text{-}St$$

$${}^3(PPS)^* + c\text{-}St \xrightarrow{k_t} (PPS) + {}^3St^* \qquad\qquad {}^3St^* \xrightarrow{k_4} c\text{-}St$$

where (PPS) stands for the polymeric -or monomeric- photosensitizer, t- and c-St are the trans and cis stilbene ground states and ^3St represents their common twisted triplet. The following assumptions are implicit in this mechanistic scheme: a) the quantum yield for the sensitizer triplet formation is equal to one; b) the energy transfer mechanism is collisional; c) the rates of energy transfer to both cis- and trans-stilbene are diffussion controlled and characterized by the same rate constant "k_t"; d) the sum of ϕ_{CT} and ϕ_{TC} (k_3/k_3+k_4 and k_4/k_3+k_4, respectively) is unity.

The first three proposals are generally admitted for aromatic ketones having high-energy triplets when they are used as sensitizers in fluid media. The fourth has been substantiated through the work of HAMMOND et al., 1969. Finally, it is assumed that all the proposals stated above are also valid when the monomeric photosensitizer is incorporated in a polymeric matrix.

Experimental

Polyvinylacetophenone and polyvinylbenzophenone were synthesized by Friedel-Crafts acetylation and benzoylation of atactic polystyrene ($\bar{M}n$ = 67.000) by a modified MERRILL and UNRUH method. The degrees of acetylation and benzoylation were determined by UV spectroscopy. Agreement with measurements carried out with other techniques (NMR, IR and carbon-hydrogen combustion analysis) was good.

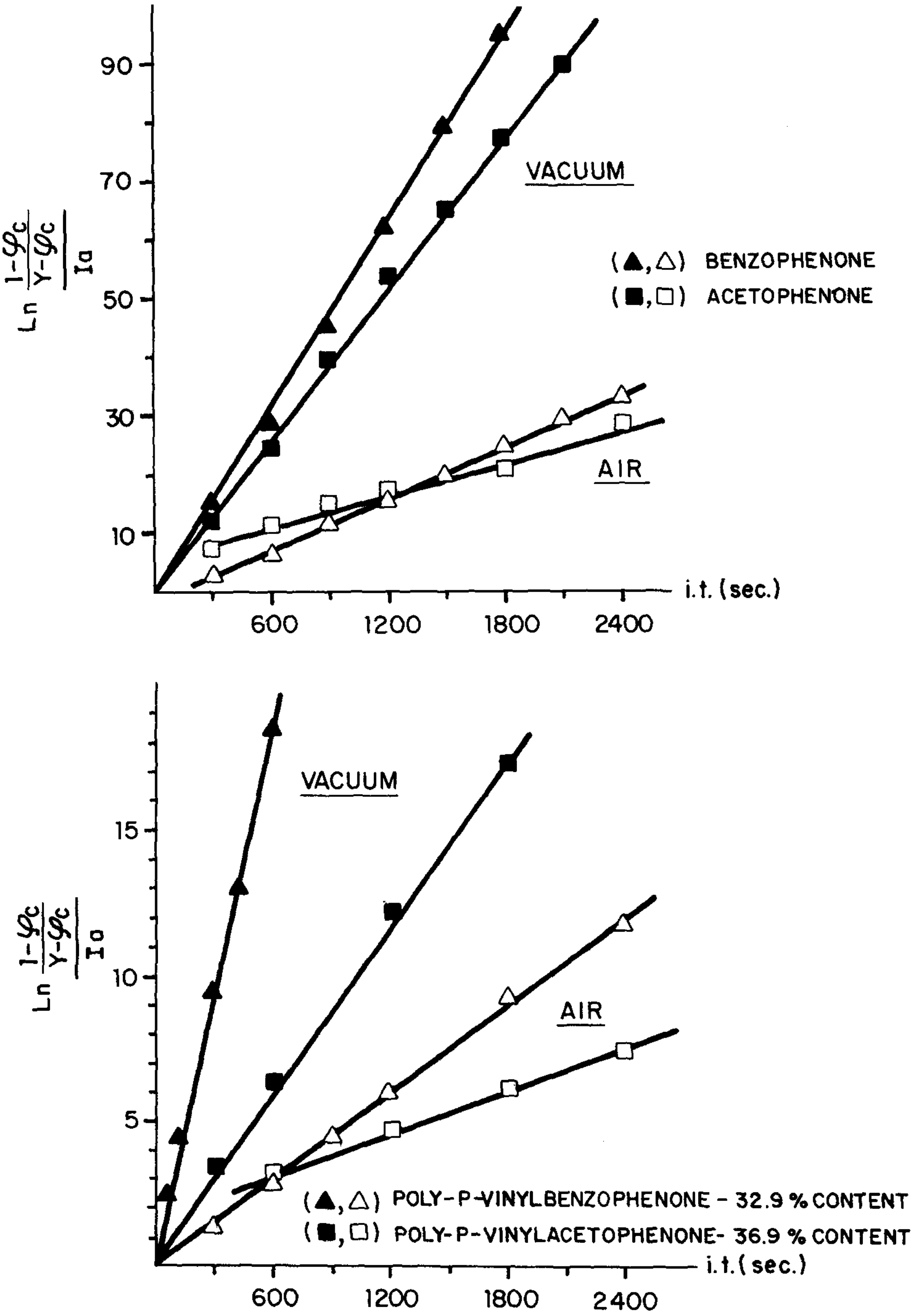
The irradiation device consisted of an optical bench including xenon lamp, monochromator, quartz lens, light filters and a cell holder thermostatized at 30°. A radiometer placed immediately behind the cell let any change in the intensity of light be known. Potassium ferrioxalate actinometry was used to relate the digital display of the radiometer to an absolute value for the number of quanta incident per unit time. Benzene solutions of the photosensitizer and trans-stilbene were irradiated with light of 360 nm. Blank tests carried out from time to time in the absence of the sensitizer showed that no direct photoisomerization took place, checking in this way the light filtering system. For experiments in an oxygen-free atmosphere, the solution contained in a pyrex-glass tube joint to the quartz cuvette (1 cm. optical path), was degassed with three freeze-degas (about 10^{-4} mm Hg)-thaw cycles. In other experiments the samples were irradiated in the same quartz cuvettes as before but open to air. Check controls showed that no reaction in the dark occurred during the working up of the samples. The kinetics was run by taking readings of absorbance at 325 nm at different times of irradiation. After the spectrophotometric readings, the samples were again placed in the holder and left to reach the equilibrium temperature (30°) before restarting irradiation. When the experiment was ended up, the solution was poured into a large excess of methanol and the precipitated polymer recovered. No significant degradation of the isolated polymer was observed.

Results and Discussion

A series of irradiations were first conducted in order to verify the complete experimental device. Photostationary trans/cis stilbene compositions were determined for the benzophenone and acetophenone sensitized photoisomerization. Coincidence with data in the literature was observed and a value of 0.45 for ϕ_{CT} was finally adopted and, consequently, introduced in (2) for the polymer-bound and free photosensitizers.

Some of the experimental plots obtained for irradiations carried out at 30° in benzene with free acetophenone and benzophenone and with their polymers are shown in figs. 1 and 2. As it can be seen, they fit well with relation (2). The linearity is also fulfilled in the other runs not shown. Coefficients of linear regression better than 0.99 were allways attained. In all the cases, the stilbene concentration was 10^{-4} M and the one corresponding to the photosensitizer around 10^{-3} M.

Since the use of polystyrene-based sensitizers, such as those we are dealing with, could give rise to interactions between the excited chromophoric group and the polymeric chain (for instance, the benzilic hydrogen is easily abstractable), we determined k_{SV}-values for acetophenone but carrying out the energy transfer processes in the presence of added amounts of polystyrene. Fig. 3 depicts the variation of k_{SV} in



Figures 1 and 2. Some of the experimental plots obtained for irradiations carried out at 30° in benzene with free and polymer-bound photosensitizers polystyrene-enriched benzene solutions. When k_{SV} is compared against the inverse of viscosity, a linear relationship is found for viscosities not higher than 5 cp. As, on the other hand, no significant amount of degraded polystyrene nor reduced ketone was produce under these conditions, we feel that the viscosity effect is the only one induced by the presence of polystyrene.

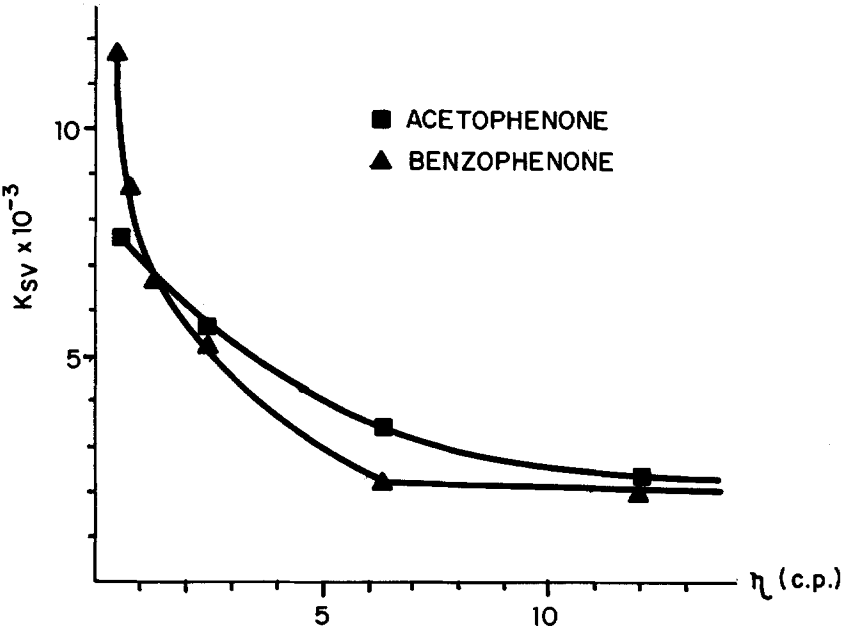


Figure 3 . Variation of Stern-Volmer constants (k_{SV}) with viscosity (η)

The whole set of results is tabulated in the Table, along with the chromophoric content of the samples assayed. Those corresponding to poly-p-(vinylbenzophenone) with a 2.7 % content gave solutions in which the viscosity began to differ appreciably from benzene. In all the other cases, the polymer solutions had practically the same viscosity as the pure solvent. For this reason, k_{SV}-values of the former have to be compared to the other values with some caution. From inspection of these data, it can be concluded that the free sensitizers are better energy donors than the polymer-bound ones. Whereas to a less extent, it appears that increasing of chromophoric content impairs the energy transfer ability of the polymeric photosensitizer. This effect, which is quite clearly shown in the results coming from the experiments made under vacuum, is not apparent when air is present. Obviously, the presence of air must lead to an oxygen-quenching process on the ketone triplets and, consequently, to a new deactivation rate constant

$$k'_d = k_d + k_{Ox} [O_2] \qquad (3)$$

TABLE

Donor	Sensitizer % content	k_{SV} values (M^{-1} x 10^{-3})	
		air	vacuum
Free benzophenone	--	1.38	11.77
Poly-p-vinyl-benzophenone	2.7	0.45	6.64
Poly-p-vinyl-benzophenone	32.9	0.51	4.13
Poly-p-vinyl-benzophenone	66.9	0.65	3.41
Free acetophenone	--	0.97	7.67
Poly-p-vinyl-acetophenone	6.5	0.29	1.47
Poly-p-vinyl-acetophenone	36.9	0.25	1.01

The lower k_{SV}-values obtained with undegassed samples might be justified in this way. The oxygen leveling effect, on the other hand, suggests that the differences in k_{SV}-values found in the polymeric samples proceed principally from differences in k_d-values. Prevalence of the quenching over the normal decay process $-k_{Ox}[O_2] \gg k_d-$ would then explain such a leveling effect.

In principle, the rate constants k_d and k_t might be approximately estimated considering both series of experiments. Thus, for each couple of k_{SV}-values, the equality (4) can be stated.

$$\frac{k_{SV}\ (\text{vacuum})}{k_{SV}\ (\text{air})} = \frac{k'_d}{k_d} = \frac{k_d + k_{Ox}[O_2]}{k_d} = 1 + \frac{k_{Ox}}{k_d}\ 1.6\ 10^{-3} \qquad (4)$$

where the last figure has been taken as the concentration (M) of molecular oxygen in air-saturated benzene. The estimations made in such a way will depend, of course, on the value given to k_{Ox}, the oxygen quenching rate constant. This constant can be estimated in turn from values reported in the literature (CLARK and STEEL, 1971; MERKEL and KEARNS, 1973), refering to the free sensitizers, benzophenone and acetophenone, although solvents different from benzene were used. Taking k_{Ox} as 1.5 10^9 M^{-1} sec^{-1} for the first ketone and 3.0 10^9 M^{-1} sec^{-1} for the second one, the respective k_d-values will be 0.32 10^6 sec^{-1} and 0.69 10^6 sec^{-1}. The corresponding two k_t-values will be then 3.8 10^9 M^{-1} sec^{-1} and 5.3 10^9 M^{-1} sec^{-1}.

Application of formula (4) to the other couples of k_{SV}-values (i.e., to the polymer-bount sensitizers), appears to us as rather unrealistic because we lack a reliable value for k_{Ox}. For this reason, it is necessary to determine the life-times of the polymer-bound triplets before a thorough analysis of the k_{SV}-values can be made. A question, on the other hand, which arises whenever Stern-Volmer constants are dealt with.

Conclusion

An experimental procedure to detect and to measure small differences in the sensitizing ability of free and polymer-bound photosensitizers has been developed. Following this procedure, free acetophenone and benzophenone were found to be more efficient than the corresponding polymer-bound ketones. Quantitative energy transfer evaluation of these polymeric photosensitizers is considered to be a necessary step in order to promote their use in the field of photochemical synthesis and, particularly, in the forthcoming development of chemical-based energy storage systems.

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