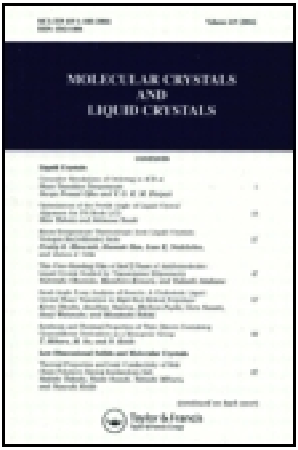

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On the vacuum ultraviolet excited luminescence of pure and doped polystyrene*

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Abstract—The overall fluorescence yield and fluorescence spectrum of polystyrene as well as the fluorescence yield of solid solutions of anthracene and of diphenyloxazole in polystyrene are studied as a function of excitation wavelength in the region 584–3000 Å. In all cases a strong dependence of the investigated properties on excitation wavelength is found.

The fluorescence yield and spectrum of polystyrene in solution is basically different from that of the solid phase. For the fluorescence yield of the solid two basic types of behavior are found, depending on the preparation and treatment of the sample. The remarkable dependence of the fluorescent spectrum of solid polystyrene on excitation wavelength is also strongly depending on the mode of preparation. In all cases there is a pronounced correlation between the absorption spectrum of polystyrene and its fluorescent properties, a greater intensity and stronger red shift corresponding to a higher absorption coefficient.

The variation in fluorescence yield of plastic solutions of anthracene and diphenyloxazole in polystyrene with excitation wavelength is very different from that for pure polystyrene. In fact for highest acceptor concentrations the former is practically opposite to the latter, indicating a strong competition between exciton transfer within the solvent and transfer to the solute.

The results indicate the decisive influence of the state of aggregation as well as of the structure of the solid on the luminescent behavior for excitation of higher electronic levels.

A. Introduction

This work was prompted by the assumption that an augmented understanding of radiation effects in organic systems may be gained by a study of the luminsecent behavior of these systems when their higher electronic levels are discretely excited. The successful use of organic solutions in scintillation counters, where their luminescence is excited

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by ionizing (α, β, γ) radiation stimulated a multitude of investigations into the nature of the scintillation process itself. In order to separate the primary effects of the incident high energy radiation from the subsequent processes which are directly connected with the emission of the characteristic luminescence of the systems (energy transfer, radiative transitions, quenching processes etc.), these systems have been studied extensively by excitation in the ultraviolet. The solvents involved were mostly simple aromatic liquids (benzene, toluene, xylene, etc.) or polymers (polystyrene, polyvinyltoluene, etc.). Excitation by UV radiation involved practically only the first excited levels of these solvents. The emission spectra of the scintillating systems (which were practically identical with those of the fluorescent solutes) were found to be the same for UV and for high energy excitation. It was also found that the dependence of the relative intensity of fluorescence of the scintillating solutions on the concentration of the fluorescent acceptor is rather similar for high energy and for UV excitation. It has thus been suggested that the final processes involved in the emission process start from the first excited level of the solvent also when the system is excited by high energy radiation, although in this case most probably higher electronic levels of the solvent are excited. On the basis of the similarities between such widely separated ranges of excitation energy it was tempting to assume that a similar behavior will be found for the whole range of excitation energies between these extremes. The elucidation of this assumption seemed to us of utmost importance for clarification of the possible mechanisms involved in the primary processes of the scintillation process and possibly of many other radiation effects as well. For this purpose we started to investigate the luminescent behavior of organic systems when their higher electronic levels are excited by radiation in the far and vacuum ultraviolet.[1] It will be seen that drastic changes in the luminescent behavior are observed when the wavelength of the exciting radiation is varied.

The present work concentrates on the luminescent behavior of pure polystyrene and of solid solutions of anthracene and of PPO in polystyrene. Polystyrene serves as a basis for rather efficient scintillation counters and its luminescent properties have been the subject of numerous investigations. Since the scintillation and luminescent properties of this material are now rather established it was hoped that the investigation of this material under vacuum ultraviolet excitation may give some basic insights in the scintillation process itself. Moreover, the absorption spectrum of polystyrene in the first electronic absorption band is rather close to that of ethylbenzene (which proves that the chromophoric elements are essentially the individual segments). On the other hand polystyrene forms solid plastics which may not behave like liquid solvents. Certain solid state effects may be expected which may be emphasized when higher electronic levels are excited. (The difference in absorption between solid and gaseous benzene increases appreciably when one goes from the first to the second absorption band[2].) It will indeed be seen in the following that structural effects are of decisive influence on the luminescent behavior of this system.

B. Experimental

1) *Preparation of samples*

The monomer (Fluka A. G.) was distilled twice in vacuo, placed in a cylindrical glass container, and deoxygenated by a repeated freezing and pumping procedure. The container was then sealed off and the material polymerized for about 90 hours at 135°C. The solid solutions of anthracene and of PPO in polystyrene were prepared in the same way only that an appropriate amount of solute was added to the monomer prior to polymerization. The material was then machined to discs of 15 mm diameter and 2 mm thickness. These discs were cut from different parts of the cylindrical polymer stubs in order to check the homogeneity of the material. Samples were cut normal to the cylindrical axis as well as parallel to it and in oblique directions.

In course of the work it was also found necessary to examine the unmachined bottom of the stubs.

A part of the machined samples were pressed by a hydraulic press (50 lb/sq. in); others were polished by different methods (e.g. on carborundum, on filter paper soaked with alcohol, etc.). Still other samples were rinsed with benzene or other liquids which dissolve polystyrene. This was done with machined samples as well as with the unmachined samples of the bottom part of the stubs.

Films of polystyrene were prepared by dissolving the material in benzene and pouring the solution on a clean surface of water. Upon evaporation of the benzene, films of polystyrene were formed. No emphasis was laid on their uniformity as to thickness. The average thickness of the films ranged between 0.1–0.5 mm.

Solutions of polystyrene were prepared by dissolving a fraction of a machined disc in an appropriate amount of very pure cyclohexane (Matheson, Coleman & Bell, spectroquality) to give a volume ratio of about 1 : 1000.

2) *Optical Arrangement*

The samples were excited by radiation from a strong continuously operating Hanovia (open end) lamp. This source was filled with He for excitation in the region 584–1950 Å. For excitation in the region 1950–3160 Å the lamp was used with air as the discharge medium. In several experiments samples were excited by radiation from a low pressure mercury lamp. The radiation was monochromatized by a Jarrell-Ash 1/2m Seya-Namioka type vacuum monochromator which, even for relatively wide slits (250μ) still gave a sufficiently well defined excitation wavelength for our purposes.

The luminescence was either directly measured by an EMI 6255 B photomultiplier (spectral response Type S 13) or passed through a Bausch and Lomb monochromator in order to measure its spectral distribution. In this case the light was usually so weak that the slits of the second monochromator had to be widely opened. The fluorescence spectra to be reported later on are thus of rather low resolution and should be regarded a mere qualitative representation of the effects.

The intensity of the exciting radiation was monitored by the fluorescence of a layer of sodium salicylate coated on a glass window.

The solutions of polystyrene in cyclohexane were placed in a vacuum tight LiF cell. This cell has been described in detail elsewhere.[3] Prior to measurement the solutions were deoxygenated by argon.

C. Results and Discussion

1. *Excitation Spectrum of Polystyrene*

a. Polystyrene in Solution

Figure 1 shows the excitation spectrum (i.e., variation of normalized fluorescent yield with excitation wavelength) for solutions of polystyrene in cyclohexane. In the region of longer wavelengths the curve extends

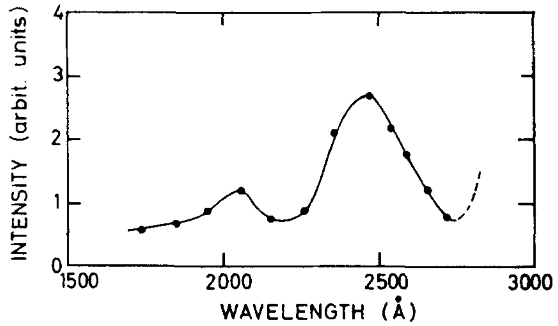

Figure 1. Variation with excitation wavelength of relative fluorescent quantum yield of solutions of polystyrene in cyclohexane.

to the absorption limit of polystyrene (the broken line indicates transmitted exciting radiation); the shorter wavelengths part extends down to about 1800 Å at which wavelength the absorption of the exciting radiation by the solvent (cyclohexane) starts to compete with that of the dissolved polystyrene. Similar results are obtained for a rather wide range of concentrations. Identical results are obtained for polystyrene from which residual styrene monomer has been removed by precipitation of the polystyrene by alcohol.

This spectrum is certainly worth a closer examination. Here we confine ourselves to pointing out one feature of the spectrum: the decrease in quantum yield when the excitation wavelength decreases below about 2500 Å, though a small peak at about 2050 Å is observed. This behavior resembles qualitatively the behavior of liquid benzene, for which the quantum yield decreases considerably when the excitation wavelength is lowered so that the second electronic band is excited, and even more so for excitation of the third band. This behavior is entirely different from that of solid polystyrene.

b. *Solid Polystyrene*

Figure 2 shows the excitation spectrum of a several weeks old machined sample of polystyrene. Figure 3a shows the excitation spectrum of a fresh machined sample. This type of behavior we call Type A. Figure 3b shows the excitation spectrum of the bottom part of a fresh polystyrene stub, when its unmachined side is irradiated by the exciting radiation. This type of behavior we call Type B. Curves *a′* and *b′* show the respective excitation spectra for "aged" samples. Figure 2 represents thus the curve for such an "aged" sample.

Comparison of the figures for solid polystyrene with that for polystyrene in solution shows the remarkable difference between the excitation spectra of the two, particularly for excitation at shorter wavelengths. Whereas the quantum yield of the solution decreases with decreasing wavelength down to 1800 Å, a sharp increase for the solid is observed. The quantum yield reaches its maximum at about 1900 Å, then decreases with decreasing wavelength and reaches a second maximum, the position of which depends to a certain degree on the age of the sample. Beyond the second minimum the quantum yield increases continuously with decreasing wavelength down to 584 Å (the lower wavelength limit of our excitation source). Comparison of the intensity at this excitation wavelength with the maximum intensity for excitation in the first absorption band shows an increase in quantum yield by a factor of 8. In certain samples this factor was even greater. The curve for Type B behavior

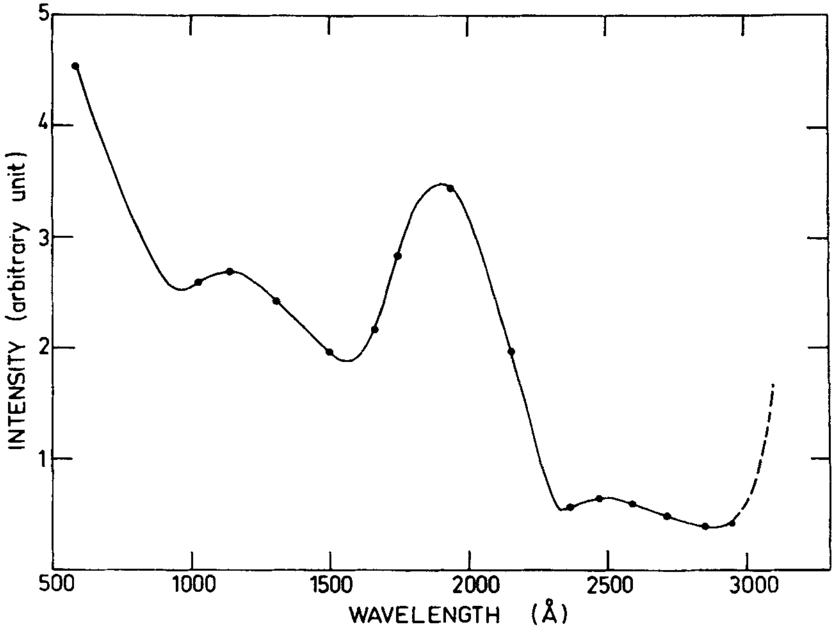

Figure 2. Variation of relative fluorescent quantum yield of solid polystyrene with excitation wavelength for a several weeks old machined sample.

(Fig. 3b) resembles rather closely that for Type A down to wavelengths of about 1500 Å. For shorter excitation wavelengths, however the difference between the two becomes obvious. The great increase in quantum yield towards the shortest excitation wavelengths seen in Type A is not observed for Type B.

In order to find out whether the Type B behavior of the "untouched" lower surface of the polymer stub represents the "true" excitation spectrum of solid polystyrene, while Type A includes effects introduced by

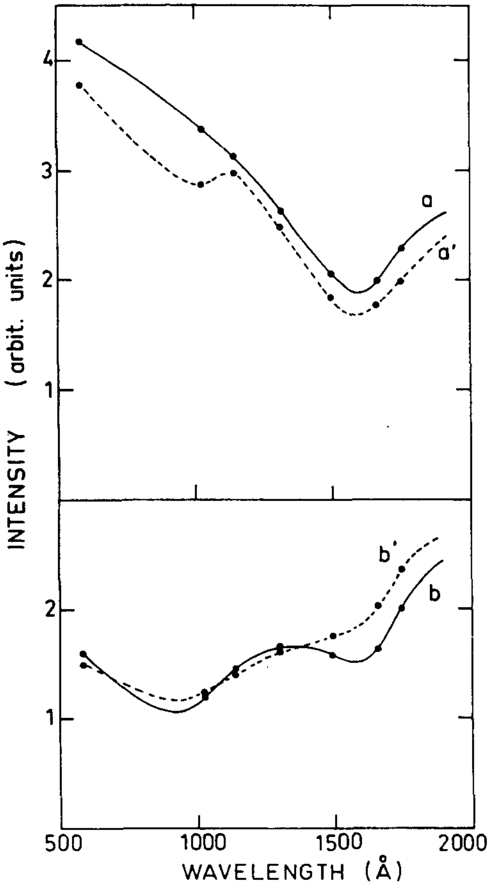

Figure 3. Variation of relative fluorescent quantum yield of solid polystyrene with excitation wavelength. Curve a: fresh machined surface. Curve a′: same surface after several weeks. Curve b: unmachined surface of freshly polymerized polystyrene stub. Curve b′: same surface after several weeks.

the machining of the sample, the surfaces of several of the machined samples were rinsed with benzene (and other solvents of polystyrene). By visual examination as well as observation under a microscope it was made sure that all the traces of the machining grooves were eliminated. The excitation spectrum of the rinsed (and dried) samples remained still Type A. In certain cases the increase in fluorescent yield at 584 Å was even greater than that for the original machined surface.

Type A behavior was found also for all films (with one exception) which were produced in the described manner.

After application of high pressure (see section B) on samples which showed Type A behavior, the behavior changed to Type B.

No change in behavior was found whether the sample was stored for a very long time in air or kept in an evacuated container. Heating of the samples, up to temperatures close to the melting region and cooling to room temperature did not change the excitation spectrum. The absolute values of the quantum yield at the various exciting wavelengths decreased, *however, considerably after this treatment.*

Prolonged exposure of our samples to the relatively weak monochromatic exciting radiation used throughout the whole work did not cause any detectable change in their luminescent behavior.

During the first few days after the preparation of the samples the overall quantum yield increases somewhat and afterwards decreases again. Over extended periods the ageing effect described in Fig. 3 is observed. Renewed machining of not too old a sample almost fully annihilates the "ageing" effect and restores the original Type A behavior (curve a). A very slow, but nevertheless pronounced ageing effect is also observed in the near UV part of the excitation spectrum. The relatively flat part of the excitation spectrum in the region of the first absorption band shows a peak at about 2500 Å, which increases with time until (after 2 years) it becomes comparable to the intensities obtained for excitation at 1900 Å. Generally it seems that the material undergoes structural changes over long periods of time and that for our purposes it is best considered to be a very viscous liquid. The effect of the application of high pressure on the sample is thus to be understood as the result of a very long lasting (or irreversible) change in the structure of the material.

At the present time it does not seem possible to give an explanation for all the facts described above. An interesting relation may however be pointed out. This is the striking correlation between the absorption spectrum of polystyrene[4] and its excitation spectrum, a higher quantum yield corresponding to a greater absorption coefficient. This correlation holds for Type A behavior down to the shortest known region of the absorption spectrum (1100 Å).

We do not discuss here the several possible mechanisms which can be forwarded in order to explain the present results. We tend to explain the results by intermolecular interactions which lead to the formation of excimers. By the term excimer we do not intend to exclude phenomena of excitation resonance or charge resonance in which more than two segmer parts of polystyrene take part. The nature of these excimers will depend on the distance between segmers and their relative position. We assume that the probability for the creation of certain types of excimers will be different for excitation with different wavelengths, depending on the transition moments of the system at these wavelengths.

2. *Emission Spectrum of Polystyrene*

Figure 4 shows the uncorrected emission spectrum of the machined surface of a polystyrene disc (thickness 2 mm) as a function of excitation wavelength. The intensity scale varies from curve to curve. The great variation of the luminescence spectrum with excitation wavelength is noted. Excitation in the wavelength region 2537–2348 Å yields the known spectrum of solid polystyrene. For excitation at 2150 Å, however, the relative intensity of this band becomes much reduced, and two additional bands, with peaks at about 3300 Å and 3900 Å appear. For excitation at 1850 Å the distribution of intensities is so strongly altered that practically only one peak, at 3800 Å is observed. With further decrease of excitation wavelength the peaks at 3150 Å and 3300 Å appear again, at different ratios; the peak at 3800 Å being relatively stronger for excitation by 1215 Å than by 1607 Å.

Polishing of the surface or rinsing with solvents of polystyrene which abraded the machined surface of the sample did not cause any appreciable change. Moreover, the unmachined bottom of the stubs, for which the excitation spectrum was found to differ considerably from that of the machined surface, showed the above emission spectra for the respective excitation wavelengths.

A rather interesting behavior is found for films. Films which were produced by evaporation of a solution of polystyrene in benzene on a water surface showed the above dependence of emission spectrum on excitation wavelength. On the other hand when cyclohexane was used as a solvent for polystyrene the longest wavelength peak of the emission spectrum (3800 Å) was not observed for any excitation wavelength. For excitation at 1850 Å the emission spectrum consists of a single band with maximum at 3400 Å.

A very pronounced effect of melting of the sample is noted. When a disc which showed the behavior described in Fig. 4 is molten by heating and cooled to room temperatures, the peak at 3800 Å does not appear. When the surface of such a sample is machined again the original behavior of the disc returns (peak at 3800 Å). When the machined surface is abraded by a dissolving liquid the behavior is again that of the "molten" sample.

The experiments show clearly the decisive influence of the solid state structure of polystyrene on its luminescent behavior. It is our assumption that the mode of polymerisation of our samples yields preferently certain local arrangements which are responsible for the observed spectra.

The influence of structure on the spectral behavior becomes evident also from the dependence of the emission spectra of the films on the nature of the solvent from which they have been drawn. It is a well known fact that films drawn from different solvents may have quite distinctly different microscopic structures.

Again we explain the different emission spectra for the different excitation wavelengths (Fig. 4) by the formation of excimers of various integer-segmer distances and/or symmetries. For excitation in the first electronic band of the phenyl segmer exciton interactions are relatively weak, though excimer formation supported by charge transfer interactions is not an infrequent process. The luminescence spectrum for excitation in the 2540–2350 Å region is thus composed of the monomeric spectrum, of an excimer spectrum of polystyrene and most probably also of the spectrum of the residual styrene monomer, which originates from direct absorption of the exciting radiation by the monomer and from energy transfer from polystyrene. For excitation at 2150 Å, the transition moment is so high that mixing of exciton interactions with charge transfer interactions makes excimer formation a prevalent process. This is seen by the strong increase of the 3300 Å band. The reduction of the peak at 3150 Å may have two additional reasons: (1) the practical

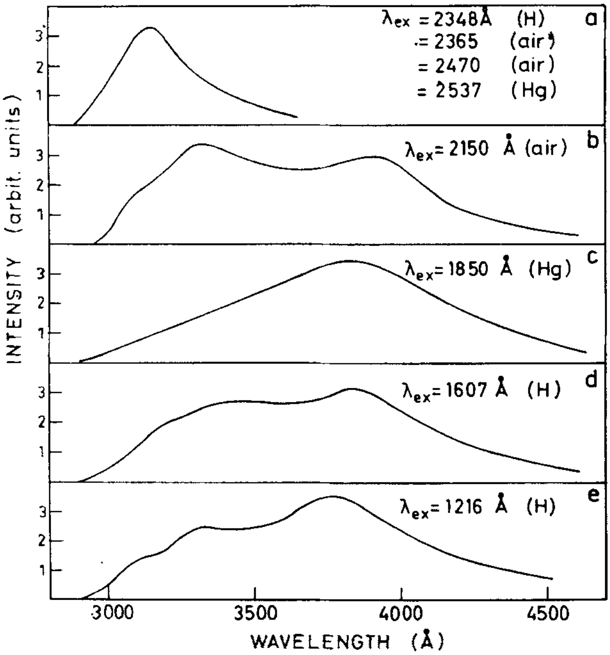

Figure 4. Emission spectrum of solid polystyrene as function of excitation wavelength. Intensity scale differs from curve to curve.

annihilation of direct absorption of the exciting radiation by styrene and (2) a considerable decrease of energy transfer from polystyrene to styrene. The peak at 3900 Å is most probably identical with the peak at 3800 Å observed for excitation at the three shorter excitation wavelengths; its apparent shift may be due to its superposition upon the spectrum of the "regular" excimer. We believe that this band represents the luminescence of an excimer of different segmer distance and/or different symmetry which is created at high probability when high transition dipole moments are involved and certain necessary (yet unestablished) structural conditions are met. Again, it is possible that the luminescence is due to the participation of more than two segmers, i.e., an exciton extending over a region of some local crystalline order.

The emission spectrum for excitation at 1605 Å resembles more the spectrum which is obtained by excitation at 2150 Å than that for excitation at 1850 Å (reappearance of the peaks at 3150 Å and 3300 Å). The absorption coefficients of polystyrene for 2150 Å and for 1605 Å are smaller than that for 1850 Å. This fact suggests the empirical rule that it is not so much the energy of the exciting photon as the transition probability of the system at the excitation wavelength which determines the behavior of the emission spectrum. This rule seems to be supported by the change in the emission spectrum when the exciting wavelength is lowered to 1215 Å. The longer wavelength portion of the emission spectrum appears relatively increased when compared with the spectrum for excitation at 1605 Å. The behaviour for excitation at 1215 Å resembles thus more that for excitation at 1850 Å than that for excitation at 1605 Å. Again, the absorption coefficient at 1215 Å is higher than that for 1605 Å (but still lower than that for 1850 Å, which seems to support the above rule).

We would like to suggest a possible application of the results for the investigation of excitation processes by high energy (β, γ) radiation. The dependence of the emission spectrum on excitation wavelength may provide a direct method for the determination of the nature of the excited states which are created when an energetic particle passes through the material. If higher levels are excited by the passage of the particle according to the Weizsaecker-Williams relation[5] or by secondary electrons, these states should contribute considerably to any subsequently emitted fluorescence by the sample; if one considers the high quantum yield for excitation by wavelengths as short as 584 Å. In order to obtain some kind of distribution function of the excited states for a given particle and material one would have to analyze the emission spectrum of the material when it is excited by the particle, in terms of the emission spectra which are obtained by excitation at the various wavelengths. The methodical development of such a procedure would certainly require a considerably better resolution of the emission spectra than that ascribed to the above results; qualitative results may perhaps be derived without much improvement.

3. *Energy Transfer from Polystyrene to PPO and to Antracene*

Figure 5 shows the relative quantum yield of solid solutions of PPO in polystyrene as function of the excitation wavelength for various concentrations of the solute. The broken curve in this figure shows the dependence of the relative quantum yield of pure polystyrene on excita-

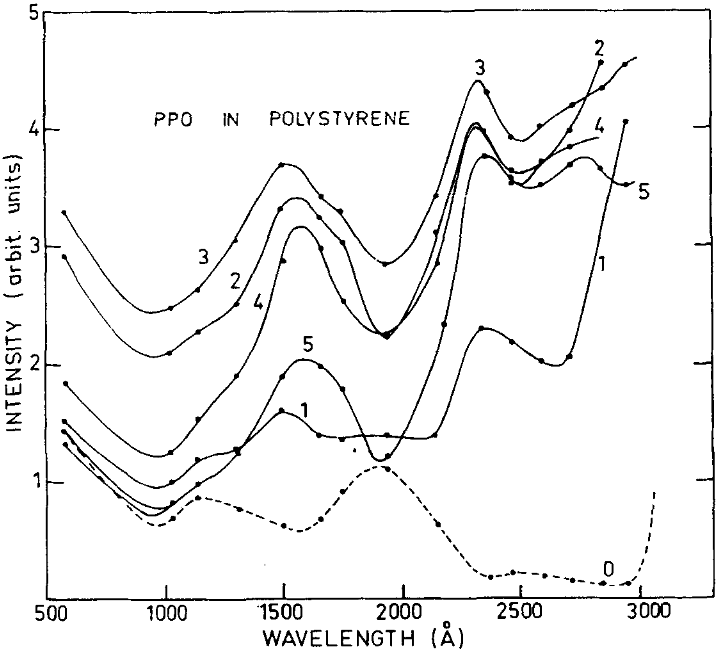

Figure 5. Variation of fluorescent intensity of solid polystyrene (dashed curve) and of solid solutions of PPO in polystyrene with excitation wavelength for different concentrations of the solute. Concentrations in moles of solute per liter of styrene monomer: 1: 0.01 2: 0.05 3: 0.01 4: 0.20 5: 0.30

tion wavelength. The difference in behavior between the pure solvent and the solid solution is obvious. In fact, quantitatively, their behavior may said to be opposed throughout a wide range of excitation wavelengths, down to 1000 Å. For excitation wavelengths for which the quantum yield of the pure solvent shows a maximum the spectrum of the solution shows a minimum and vice versa. These spectra have been obtained for machined discs of the solid solutions. The same results are obtained for the unmachined bottom of the stubs. The same results are also obtained for films of PPO in polystyrene.

The emission spectrum of all the samples which contained PPO was solely that of the solute, for all excitation wavelengths.

The results seem to confirm our qualitative explanation of the luminescent behavior of pure polystyrene as a function of excitation wavelength, by interactions between an excited segmer and its neighbor (or neighbors). In the solid solutions the concentration of the solute is such that for all excitation wavelengths below 2000 Å only a very small fraction of the exciting radiation is adsorbed by the solute. Excitation of the solute by direct absorption is thus negligible and practically all the observed fluorescence is due to a transfer of excitation energy from the solvent (polystyrene) to the solute. The results show thus a strong dependence of the energy transfer on excitation wavelength. This behavior may now be understood in terms of a competition between intermolecular interactions within the solvent (polystyrene) and interactions between the solvent and the solute which result in the transfer of excitation energy to the latter. The solute subsequently emits its own characteristic fluorescence. If the excitation wavelength is such that polysyrene excimers are readily formed (depending also on the microscopic structure of the sample), energy transfer to the solute is reduced and vice versa.

Figure 6 shows the relative quantum yield of machined samples of solid solutions of anthracene in polystyrene as function of the excitation wavelengh for various concentrations of the solute. (Again the broken curve represents the results for pure polystyrene.)

A comparison of the curves for the solutions of anthracene with that for pure polystyrene and those for solutions of PPO leads to an interesting conclusion, namely that the former is a superposition of the latter two. The curves for the solutions of anthracene show a set of maxima which coincide with those for pure polystyrene and others which coincide with those for solutions of PPO. It is also seen that for higher concentrations the behavior of the anthracene solutions resembles more that of the solution of PPO whereas a more polystyrene-like behavior dominates for lower concentrations of anthracene. (The high peaks for excitation at 2550 Å are certainly due to direct absorption of the excitation energy by the solute, the absorption coefficient of anthracene at this wavelength being several orders of magnitude higher than that of polystyrene.)

Again the emission spectrum of the anthracene solutions was solely that of the solute.

This behavior seems to indicate a competition between two mechanisms of energy transfer, one which is similar to that which determines the efficiency of energy transfer to PPO and another process in which anthracene seems to play the role of a polystyrene segmer. The nature of this process is unknown. It may possibly be connected with the parti-

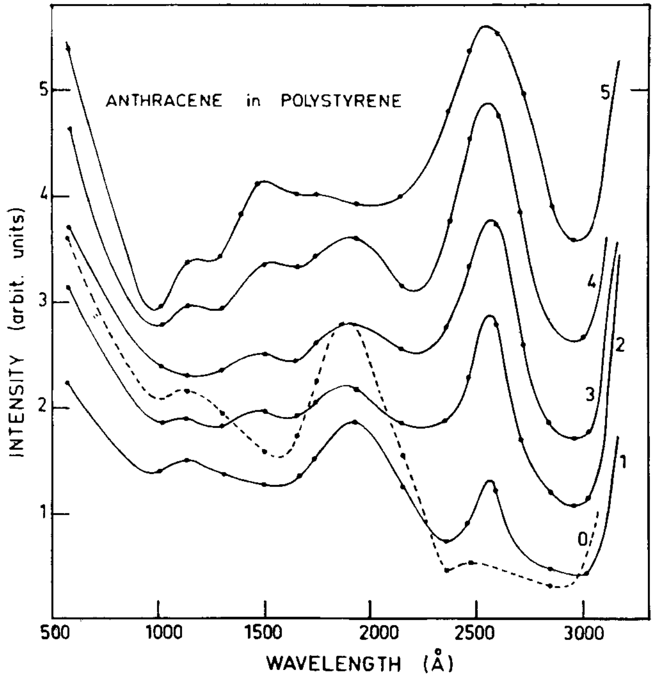

Figure 6. Variation of fluorescent intensity of solid polystyrene (dashed curve) and of solid solutions of anthracene in polystyrene with excitation wavelength for different concentrations of the solute. Concentrations in moles of solute per liter of styrene monomer:
1: 0.01 2: 0.05 3: 0.10 4: 0.20 5: 0.45

cular way in which anthracene is incorporated in the polymer matrix. It has been shown by various authors that some kind of physical binding between anthracene and the polymer chains exists when anthracene is introduced into the styrene monomer before polymerization[6,7]. A possible mechanism which would explain the appearance of these maxima which coincide with those for pure polystyrene is radiative transfer, i.e. reabsorption of the polystyrene fluorescence by anthracene. The relative contribution of this effect to the observed fluorescence intensity of anthracene will be higher the lower the "true" energy transfer by intermolecular interactions between the polymer and anthracene, and the higher the fluorescence intensity of polystyrene. Both conditions will be met more readily at lower concentrations of anthracene. It is indeed seen from Fig. 6 that the polystyrene-like maxima are more pronounced at lower solute concentrations. Whether radiative transfer is of importance at these still rather high solute concentrations can possibly be decided by decay time measurements. (For excitation by electrons radiative transfer has been found to be the main transfer process at very low concentrations of anthracene.)[8]

Figure 7 shows the transfer efficiency for the solid solutions of PPO in polystyrene as function of the concentration of PPO. The concentration is given in moles of solute per liter of styrene monomer. The ordinate gives the normalized fluorescence intensity of the solution when it is excited by radiation which almost exclusively absorbed by polystyrene, divided by the (normalized) intensity which is obtained by excitation with radiation of 3130 Å for which polystyrene is transparent, but which

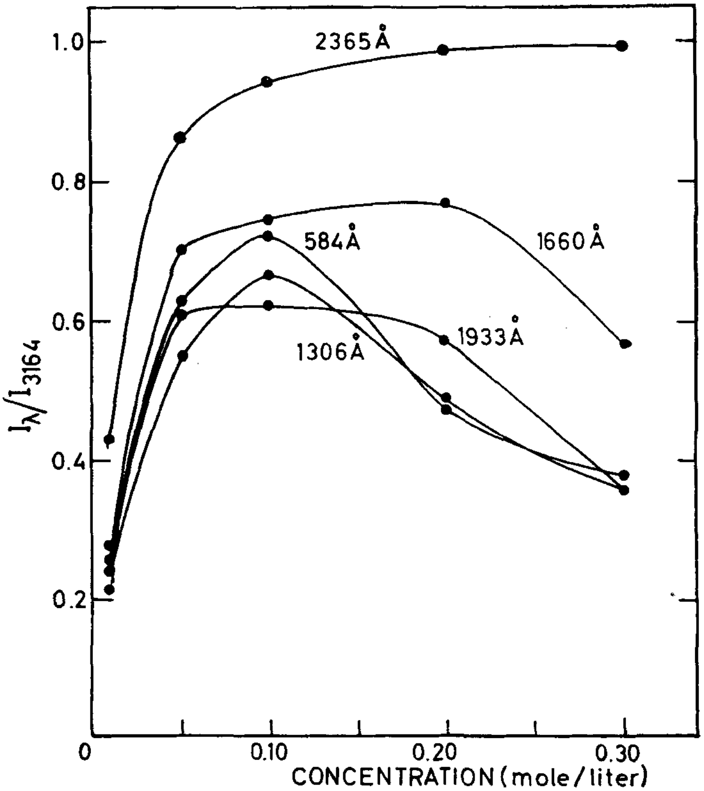

Figure 7. Efficiency of energy transfer in solid solutions of PPO in polystyrene as function of concentration of solute, for different excitation wavelengths.

is strongly absorbed by PPO. It is seen that for different excitation wavelengths different curves are obtained. In particular it is noted that for shorter excitation wavelengths the transfer efficiency decreases with increasing acceptor concentration, beyond a certain concentration. It can hardly be assumed that the probability for energy transfer interactions between an excited segmer and the neighboring solute molecules decreases with increasing number of these molecules. This is certainly true for a single solvent molecule—single solute molecule interaction. In a solid system, however, the structural conditions may be altered by the introduction of a high concentration of foreign molecules to such an extent that in spite of the increased number of acceptors, conditions for energy transfer become less favorable, and that these changes are more influential for energy transfer from higher excited levels.

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