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Fluorescence spectra of polystyrene excited by beta-rays and uv-light

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# FLUORESCENCE SPECTRA OF POLYSTYRENE EXCITED BY BETA-RAYS AND UV-LIGHT

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Monomer free polystyrene samples, produced by evaporation from a solvent excluding oxygen, show by excitation with UV-light ($\lambda = 270$ nm) or with β-rays besides the excimer peak at 330 nm (P-peak) an additional fluorescence peak at 390 nm (G-peak). This peak disappears by melting of the sample or admission of air. The influence of additives on the fluorescence spectra was investigated. 1,2-di-(2-pyridyl)-ethylene, an efficient quencner for the first excited singlet state of polystyrene, reduces the P-peak much more than the G-peak. Therefore it is inprobable that the states responsible for the P- and G-peak are excimers of different distance or symmetry of the segmers or excimers with more than 2 segmers participating. The intensity of the G-peak in comparison to the P-peak increases by addition of low concentrations of hexachlorocyclohexane ($c < 10^{-5}$ mole/l). The dependence on the structure of the polymer and the influence of the electron scavenger suggests, that the appearance of the G-peak is connected with the existence of electron traps. We assume that the origin of the G-peak is a charge separate state analogous to that proposed by Janssen and Funabashi to explain the luminescence in γ-irradiated alkane glasses.

1. INTRODUCTION

By excitation of polystyrene in its first absorption band (240–270 nm) one or two structureless fluorescence peaks wity maximas at 290 nm and 330 nm were observed.[1–4] These two peaks have been attributed to the monomer-(S-peak) and excimer fluorescence (P-peak) of polystyrene.

$$S^* \rightarrow S + h\nu_{mon}$$
$$S^* + S \rightarrow S_2^* \rightarrow 2S + h\nu_{exc}$$
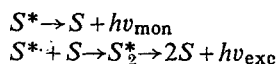
At 70 °K only the S-peak is observed. At this temperature during the lifetime of the excited state the parallel arrangement of phenylrings, necessary for excimer formation, is not achieved.[5] In pure polystyrene at room temperature, due to complete excimer formation, only the P-peak is detected. In polystyrene containing still residual styrene monomer, however, the spectrum is mainly that of the monomer (280 nm).[5,6,7] Fluorescence spectra similar to these obtained for UV-excitation obtained Koski,[8] Krenz[9] and Rozman[2] using X-rays and β-rays for excitation. On the other hand, Leibowitz and Weinreb[10] observed by excitation with vacuum ultraviolet ($\lambda < 150$ nm) an additional peak at 390 nm. Recently we found that this peak can also be detected by excitation with β-rays.[11] The aim of the present work was to obtain more information on the fluorescent states and their precursors in polystyrene excited by UV-light and ionising radiation.

2. EXPERIMENTAL

2.1. Fluorescence Measurements

The fluorescence measurements were performed with a modified PMQ II Zeiss spectral photometer. The sensitivity was increased using an EMI 6256 S multiplier.

The arrangement used for β-excitation is shown in Figure 1. Between the sample and the Sr^{90} source an aluminium foil was placed as light reflector. The intensities have been corrected for dispersion of the monochromator and spectral sensitivity of the multiplier. The true fluorescence intensity was calculated by a derivation given by Förster.[24]

The intensity of the fluorescence was very small, so that a large band width (30 nm) of the monochromator had to be used. Therefore the resolution of the spectra is low.
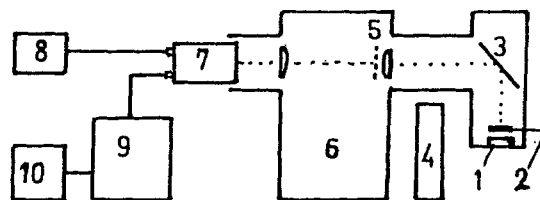

FIG. 1. Arrangement for β-excitation. (1) Sr^{90}-source (100 mC); (2) Sample; (3) Vioflex mirror; (4) Shielding; (5) Sector diaphragm; (6) Monochromator; (7) Multiplier; (8) High voltage supply; (9) Amplifier; (10) Recorder.

For UV-excitation a Xenon high pressure lamp connected with a monochromator or an interference filter (transmission maximum at 270 nm) was used. The construction of the sample holders for the β- and the UV-arrangement allows to perform measurements in nitrogen atmosphere.

2.2. Polymerization

Styrene was purified by vacuum distillation under nitrogen. Polymerisations were done by radical polymierization (120 °C; 6 d without catalyst; 80 °C, 0.3 per cent azodiisobutyronitrile and by anionic polymerization (-70 °C, sodium-naphthalenide as initiator). The polymers were purified three times by dissolving in benzene and precipitation by methanol. The last solution was dryfrozen.

2.3. Sample Preparation

(a) To dryfrozen polystyrene (30–100 mg) in containers with an aluminium foil as bottom, 1 ml of solvent or solvent containing additive in appropriate concentration was added. After dissolution the solvent was evaporated in a temperature constant container at 55 °C during 1 or 2 days. During the whole procedure air was excluded. Discs of 13 mm diameter were cut out. Such foils were 0.1–0.4 mm thick and fairly uniform.

(b) Some of the samples were produced in a hydraulic press at 200 kp/cm² and temperatures >100 °C in vacuum.

All samples were stored in nitrogen atmosphere.

3. RESULTS

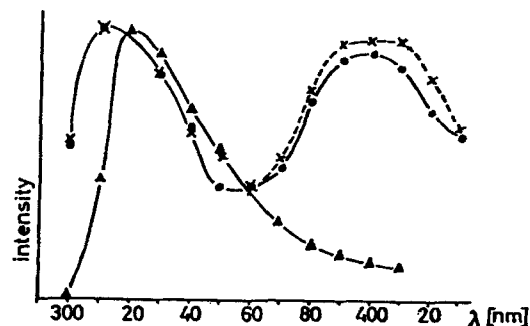In Figure 2 the spectra obtained by β-irradiation of polystyrene samples produced either by evapora-

FIG. 2. Fluorescence spectra of polystyrene. ▲ samples produced by pressing at 100°C; ● samples produced by evaporation (24 hours); × samples produced by evaporation (48 hours); solvent benzene; β-excitation.

tion or by pressing at elevated temperatures are compared.

In both cases air was excluded during preparation and irradiation. Some of the samples were evaporated a further day and the spectrum taken again.
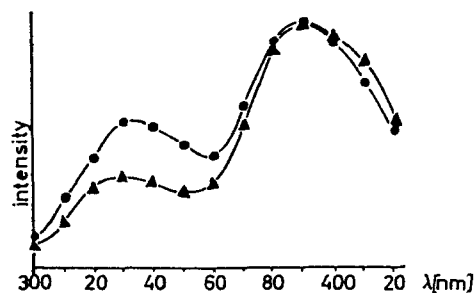
FIG. 3. Influence of the solvent on the fluorescence spectrum. ● spectrum of polystyrene dissolved in butanone and evaporated; ▲ spectrum of polystyrene dissolved in dioxane and evaporated; UV-excitation ($\lambda_{exc.}$ = 270 nm).

Figure 3 compares the spectra of samples produced by evaporation from butanone and dioxane for UV-excitation. Only evaporated samples show the G-peak. Although the ratio of the intensity at 390 to the intensity at 330 nm differs between UV- and β-excitation to some extent, the maximas are found in both cases at the same wavelength.

Figure 4 shows the influence of air admission on the spectra. In Figure 5 the intensity of the G-peak (390 nm) is plotted versus the time of air exposure. A regeneration of the G-peak by storage of the air

FIG. 4. Influence of air admission on the fluorescence spectrum of polystyrene. (a) 3 hours air admission ×; (b) 27 hours air admission ●; (c) 110 hours air admission ▲; (d) stored 5 days in nitrogen atmosphere after 110 hours air admission ■; UV-excitation ($\lambda_{exc.}$ = 270 nm); The plots are on different scale.

FIG. 5. Decrease of the fluorescence intensity at $\lambda = 385$ nm with time of air admission. UV-excitation ($\lambda_{exc.} = 270$ nm).

FIG. 6. Absorption spectrum of 1,2-di-(2-pyridyl)-ethylene, Solvent cyclohexane.

exposed samples in nitrogen atmosphere for 5 days was not possible (Figure 4d).

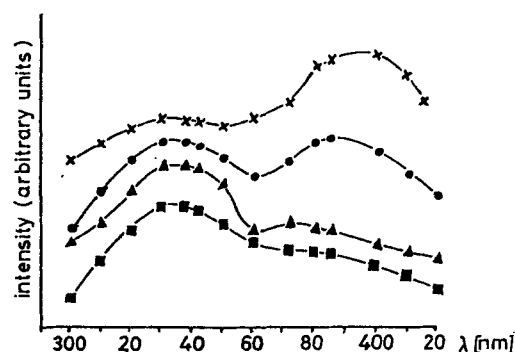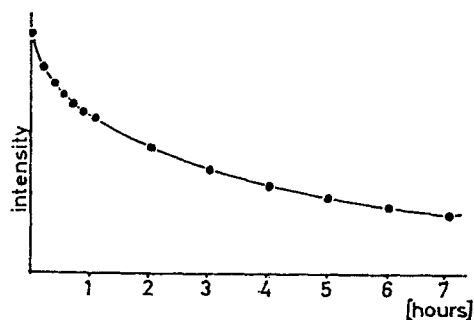Exciting with UV-light fluorescence spectra were taken from solutions of polystyrene samples, which showed in solid state the G-peak, from styrene monomer and the solvents. No fluorescence at 390 nm was detected.

As additives we used the aroxyl radical 'Galvinoxyl',† 1,2-di-(2-pyridyl)-ethylene and hexachlorocyclohexane.

Galvinoxyl up to 10^{-2} mole/l showed little influence on the fluorescence spectra. The ratio of the intensity at 390 to the intensity at 330 was found to be:

	I 390/I 330
0 mole/l	0.75
9.07×10^{-4} mole/l	0.73
9.07×10^{-3} mole/l	0.75

The absorption spectrum of 1,2-di-(2-pyridyl)-ethylene is shown in Figure 6.

In Figure 7 the fluorescence spectra of pure polystyrene and polystyrene containing $9.07 \cdot 10^{-5}$ – $9.07 \cdot 10^{-2}$ mole/l of this additive are compared and the transparence of a sample containing $9.07 \cdot 10^{-4}$ mole/l is given. The concentration of the electron scavenger hexachlorocyclohexane (HClH) was varied from 10^{-8} to 10^{-1} mole/l. The intensity of the G-peak and P-peak was determined using UV- and β-excitation. The ratio of the intensity at 390 to the intensity at 330 nm is shown in Figure 8.

FIG. 7. Fluorescence spectrum of polystyrene containing 1,2-di-(2-pyridyl)-ethylene. UV-excitation ($\lambda_{exc.} = 270$ nm); x pure polystyrene; ⊙ $9.07 \cdot 10^{-5}$ mole/; △ $9.07 \cdot 10^{-4}$ mole/l; ◯ $9.07 \cdot 10^{-3}$ mole/l; □ $9.07 \cdot 10^{-2}$ mole/l; —·— transparence (I/I_0) for a sample containing $9.04 \cdot 10^{-4}$ mole/l additive.

† R ⟨⟩ = CH – ⟨O⟩ – O.

R = tert. butyl
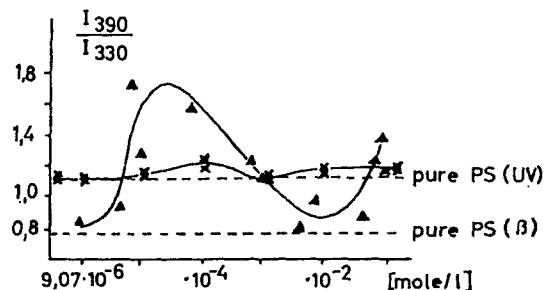
FIG. 8. Influence of hexachlorocyclohexane (HClH) on the ratio of the fluorescence intensity at 390 nm to the intensity at 330 nm. ▲ β-excitation; x UV-excitation ($\lambda_{exc.} = 270$ nm).
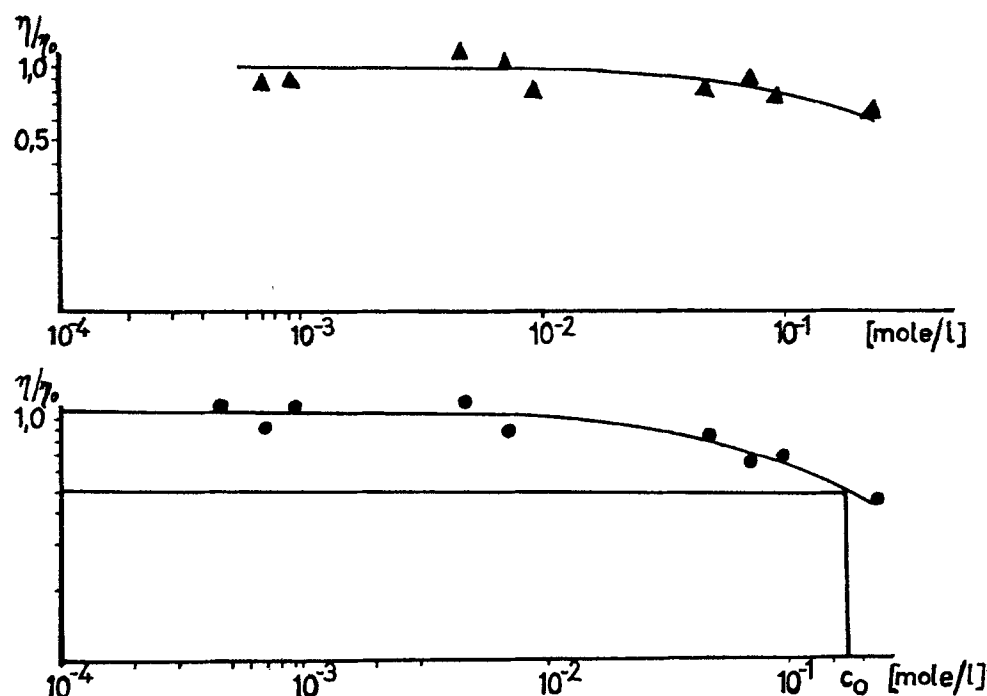
FIG. 9. Effect of HClH ($c > 10^{-4}$ mole/l) on the fluorescence intensity at 330 nm. ▲ UV-excitation; β-excitation.

HClH has no fluorescence peak in this spectral region.

Figure 9 compares the effect of HClHC $>10^{-4}$ mole/l on the fluorescence emission at 330 nm (P-peak) for β- and UV-excitation. In this concentration range HClH acts only as scavenger or quencher. A critical radius $R_w = 13.5$ Å was calculated from the experimental results for β-excitation using the formula[21]

$$R_w^3 = \frac{3 \ln 10}{4\pi N_{L} \cdot (\Delta C/\Delta \log J/J_0)}$$

c = concentration

J, J_0 = fluorescence intensity with and without scavenger

R_w: Is an excited styrene unit in the distance R_w from the scavenger than the probability for fluorescence is equal to the probability for desactivation by scavenging and quenching.

Figure 10 gives the photoexcitation spectrum of the peak at 390 nm.

4. DISCUSSION

Excited states can be produced by ionizing radiation directly in the primary absorption act or by
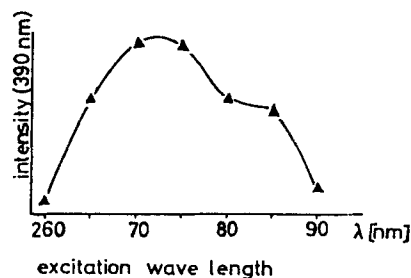
FIG. 10. Photoexcitation spectrum for the peak at 390 nm for thin polystyrene films ($\sim$0.1 mm).

recombination of the molecular ions with electrons. In order to distinguish between these possibilities we compared the influence of hexachlorocyclohexane, an efficient electron scavenger, on the fluorescence yield for UV- and β-excitation.

Reactions (1a) to (7b) (opposite) for the formation of fluorescent states in polystyrene by excitation with UV-light or ionizing radiation are to be discussed.

Reaction (3b) occurs only at high triplet concentrations along the track of an ionizing particle with large LET and can be neglected in our case.

For phenyl groups reaction (6b) is excluded by some authors[12] because swarm experiments in the gas phase showed no electron attachment to benzene. But in the condensed phase there is evidence,

that this reaction takes place. Ho and Siegel[13] detected by pulseradiolysis of polystyrene solutions an absorption band at 405 nm, which disappears by addition of chloroctane. They ascribe this absorption to the polystyrene anion. Evidence for reaction (7b) comes from the fact, that a strong increase in excimer fluorescence is observed by excitation with light > 8.47 eV, corresponding to the ionization potential of polystyrene.[14]

UV-excitation in the first absorption band

ionizing radiation

(1a) $S \xrightarrow{hv} S_i^*$

(1b) $S \longrightarrow S_{i,T}^{**} \longrightarrow S_{i,T}^*$

(2a) $S_i^* + S \rightleftharpoons S_2^*$
$\downarrow hv_{mon} \quad \downarrow hv_{exc}$

(2b) $S_i^* + S \rightleftharpoons S_2^*$
$\downarrow hv_{mon} \quad \downarrow hv_{exc}$

(3b) $S_T + S_T \longrightarrow S_2^{**} < \begin{matrix} S_2^* \\ S^* + S \end{matrix}$

(4b) $S \longrightarrow S^+ + e$

(5b) $S^+ + e \longrightarrow S^{**} \longrightarrow S^*$

(6b) $e + S \longrightarrow S^-$

(7b) $S^+ + S^- < \begin{matrix} S_2^* \\ S^* + S \end{matrix}$

S_i^*, S_T^* first excited π-singlet state and π-triplet state
S^+, S^- positive and negative molecular ions
S_2^* excimer
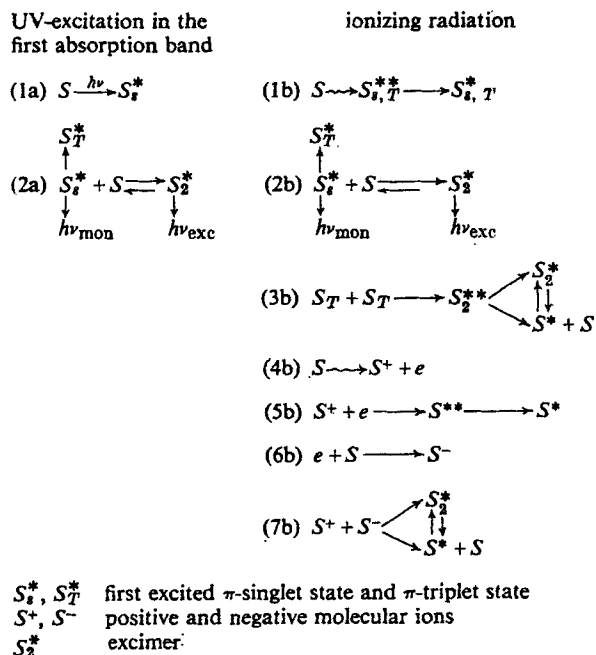
By addition of an electron scavenger reactions (6b) and (7b) are partly replaced by the corresponding reactions of the scavenger

$$F + e \rightarrow F^- \qquad (8b)$$
$$S^+ + F^- \rightarrow hv \qquad (9b)$$

A comparison of the effect of an electron scavenger on the fluorescence intensity, using β- and UV-excitation, therefore, gives information on the participation of ion recombinations for the formation of fluorescent states.

Figure 9 shows that the reduction of the fluorescence intensity by HClH for β-excitation is more effective than the quenching observed for UV-excitation. For ionizing radiation reaction (7b) therefore plays an important part.

From Figure 9b a critical radius $R_w = 13.5$ Å† for scavenging + quenching by HClH was deduced. Similar experiments with different electron scaven-

† Definition: see results.

gers in cyclohexane containing scintillators resulted in critical radia for electron-scavenging of about 30 Å.[15] For the smaller critical radius found for solid polystyrene the electronaffinity and polarizability of the phenyl groups will be responsible.

Fluorescence peak at 390 nm (G-peak)

In monomer free polystyrene samples, produced by evaporation from a solvent excluding oxygen, we observed by excitation with UV-light and with β-rays besides the excimer peak (P-peak) an additional fluorescence peak at 390 nm G-peak (Figures 2 and 3). The fact, that this peak has not been found in earlier investigations may have two reasons, Most investigations have been done with samples containing still monomer and oxygen was not excluded. In this case, due to energy transfer to the monomer, the fluorescence spectrum observed is mainly that of the monomer.[6] On the other hand, oxygen competes effectively with fluorescence emission at 390 nm. In our experiments, the G-peak decreased rapidly by admission of air and air saturated samples showed no peak at 390 nm (Figures 4 and 5). Leibowitz and Weinreb[10] observed the fluorescence peak at 390 nm only for excitation with light of energy > 6 eV. This may be due to the fact, that for these energies besides excitation also ionization takes place. Under these conditions oxygen diffusion is not effective enough to quench the fluorescence completely.

Infrared and X-ray experiments[16,17] show, that atactic polystyrene is completely amorphous with the phenylrings arranged statistically along the chain. Crystalline regions therefore can not be responsible for the observed fluorescence.

The following arguments exclude a possible attribution of the G-peak to scattered light and impurities.

The G-band was found in spite of different spectral distribution of the scattered light using a monochromator or a filter. The observed influence of oxygen on the fluorescence intensity also contradicts an attribution of the G-peak to scattered light.

Impurities can be incorporated into the polymer by the solvent, the monomer and the catalyst or can be produced by radiation. Prodcution of impurities by radiation as origin of the G-peak can be excluded, because the fluorescence intensity decreases with irradiation time.

The fluorescence spectra of the nitrogen-saturated solvents—benzene, dioxane, butanone—the monomer and solutions of polystyrene showed no emission at 390 nm.

Polystyrene was produced by radical polymerisation with ABN† as catalyst and by anionic polymerisation with sodium naphtalenide as initiator. The fluorescence spectra of the two polymers were identical, although differences in the intensities were observed. The G-peak therefore cannot be attributed to an impurity fluorescence.

The triplet state could be the origin of the emission at 390 nm. The position of this term in polystyrene is not known. In benzene the triplet term is 3.6 eV above the ground state (corresponding to 345 nm) and the transfer from S_1 to T_1 is of the same order of magnitude than the transiton S_1 to S_0, but the transition T_1 to S_0 is strongly forbidden.[19] The assignment of the G-peak to the triplet state conflicts with the fact, that it is so sensitive on preparation of the samples, a peculiarity not expected for a triplet transition. Weinreb and Leibowitz[10] determined the lifetime of the emission at 390 nm to be smaller than 0.2 msec. This upper limit makes the assignment of this spectrum to a long lived phosphorescence, originating from a triplet state, very unprobable, since it would indicate effective processes, quenching the longlived part of the triplet states. Such quenching processes would reduce the intensity and make it practically unmeasurable. Galvinoxyl is known as an effective quencher for the triplet state of benzene.[18] By addition of this aroxylradical we observed little influence on the spectrum and the ratio of the intensity at 390 nm to the intensity at 330 nm was found to be almost independent of additive concentration in the investigated range $(0-10^{-2} \text{ mole/l})$. Therefore it is unprobable that the triplet state is responsible for the G-band.

Excimer formation with more than two segmers participating, could be responsible for the G-peak. Based on calculations of Vala and co-workers[20] and Srinivasan, Russel and McGlynn[21] it would also be possible, that the P-peak (330 nm) and the G-peak (390 nm) are excimers with different segmer distance and/or different symmetry. Weinreb and Leibowitz suggest this explanation for the emission at 390 nm. To test this possibility we used 1,2-di-(2-pyridyl)-ethylene. This additive quenches the first excited singlet state of polystyrene effectively and does not fluoresce itself. If the P-peak and the G-peak correspond to different types of excimers originating from the first excited singlet state, both peaks should be quenched effectively. Figure 7 shows, that the intensity of the G-peak is reduced by this additive

† azo-di-isobutyronitrile.

much less than the P-peak. Therefore, it is unprobable that the states responsible for the G- and P-peak correspond to different types of excimers.

In order to get further information on the origin of the G-peak, we used the efficient electron scavenger hexachlorocyclohexane (HClH) as additive. In Figure 8 the ratio of fluorescence intensities at 390 and 330 nm is plotted versus the HClH-concentration. Especially for β-excitation strong dependence on the HClH concentration is observed. For concentrations $>10^{-4}$ mole/l a decrease of the ratio is observed. Such a behaviour is plausible,[21] if for β-excitation ion electron recombination is of more importance for the formation of the state responsible for the G-peak than for excimer formation. But the strong increase of this ratio in the concentration range $10^{-6}-10^{-4}$ mole/l HClH is unexpected.

As already mentioned, the G-peak is only observable in the solid polymer and the appearance of this peak is very sensitive on the manner of preparation. Samples produced by melting and pressing show no G-peak. Samples produced by evaporating solutions show the G-peak, but it disappears by heating above the glass transition point.

The dependence on the structure of the polymer and the influence of the electron scavenger HClH suggests, that the appearance of the G-peak is connected with the existence of electron traps. Already Ofran[22] assumed the existence of such traps to explain the photocurrent observed during UV-irradiation of polystyrene.

We suggest, that the origin of the G-peak is a charge separate state (CS-state) analogous to that proposed by Janssen and Funabashi[23] to explain the observed luminescence of γ-irradiated alkane glasses. The radiative transition of a CS-state to the ground state is of the same type as the fluorescence of a charge transfer state; the difference is that in a CS-state the electron is not held by a molecule but by electron-traps due to structural irregularities. The effect of HClH as additive shows, that such traps can be enhanced or replaced by an electron scavenger.

The energy of a CS-state will be given by

$$E_{CS} = I - P - C - A$$

I = ionisation potential of polystyrene
P = polarisation energy due to a pair of charges (for anion of charge q in a distance r of a neutral molecule of polarisability α the polarisation energy is $-q^2\alpha/2r$ 4)

C = interaction energy between the positive and negative charges $-q^2/r$

A = electron affinity of polystyrene.

Especially the polarisation energy is a very sensitive function of the molecular aggregation around the charges.

Necessary conditions for the occurrence of a radiative transition from the CS-state to the ground state are:

The energy of the CS-state must be lower than the energy of the first excited singlet state. Janssen and Funabashi[23] have shown from a theoretical model that this situation is possible.

Ion-electron recombination must be retarded long enough, that fluorescence can compete with this process.
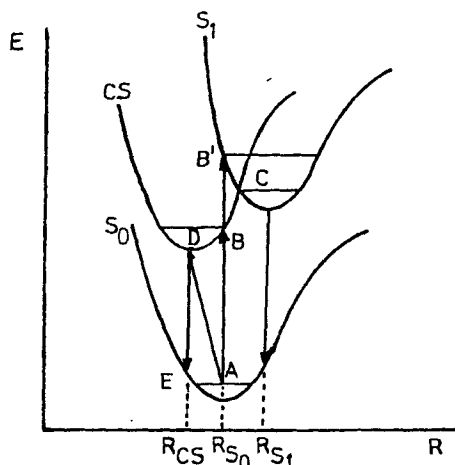

FIG. 11. Electronic energies of the system as a function of the intermolecular separation R. S_0 = ground state; S_1 = first excited singlet state; CS = charge separate state.

In Figure 11 a schematical representation of the energy of the system is given as function of the configuration coordinate R. R is the intermolecular separation between an ion and its surrounding molecules.[23]

The charge transfer state can be populated by direct excitation $A{\to}B$ and by intersystem crossing $S_1{\to}CS$ at C. For ionizing radiation including UV-light > 150 nm the formation of the CS-state is also possible via ionized states.

The photoexcitation spectrum for thin foils (0.1 nm) shows a maximum in G-peak intensity for excitation at 270 nm, corresponding to the $S_0{\to}S^*$, transition (Figure 10).

Therefore, population of the CS-state must take

place primarily by intersystem crossing $S_1{\to}CS$. This can only occur if the lifetime of the S_1-state is long enough, that the change in configuration $R_{S_1}{\to}R_{CS}$ can take place. In alkane glasses the CS-state is not detected using UV-excitation. This will be due to the fact, that the lifetime of the S_1-state in polystyrene ($\sim 10^{-8}$ sec) exceeds considerably the lifetime of the dissociative S_1 state in alkanes ($\sim 10^{-14}$ sec). For thick samples (~ 1 mm) an additional maximum of G-peak intensity was found for excitation at 340 nm, which may correspond to the non-vertical transition $A{\to}D$.

ACKNOWLEDGEMENTS

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