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Fluorescence Degradation of Polyvinyltoluene

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Degradation of monomer and excimer fluorescence is studied with irradiation by uv light. Effects of surface treatment, ambient gas and the residual monomer are examined. It is found that the degradation is accelerated by the residual monomer and oxygen. Expressions for the degradation curve are derived taking direct damage, filter effect and quenching into consideration. From the comparison of these expressions with experiments, quenching is most important for the observed fluorescence degradation. For small irradiation doses and small concentrations of the residual monomer, the degradation obeys the Stern-Volmer type equation in both monomer and excimer fluorescence. The fluorescence and absorption spectra of the samples are also observed at various irradiation doses.

§1. Introduction

Radiation damage of polymeric systems or molecular crystals has been examined by many workers with respect to radiation dosimetry. Irradiation of such materials with atomic radiations or uv light produces various changes in their optical properties. It increases their optical density,[1-3] induces photoluminescence[4,5] and reduces efficiency of their fluorescence.[6-13]

Reduction of fluorescence efficiency in polymeric systems such as polystyrene-additive fluorescent solutes has been studied to clarify the mechanisms of deterioration of plastic scintillators or of energy transfer in such systems. In polymeric systems, most of the excitation energy of atomic radiations or uv light is absorbed in the host polymer and then the excitation energy is transferred to additive fluorescent solutes. Therefore, radiation damage of the host polymer itself is important for understanding the above problems. With the exception of some descriptions for pure polystyrene,[12] investigations of fluorescence degradation of the host polymer itself have been rarely made in spite of their importance.

In the present paper, we study in detail the fluorescence degradation of polyvinyltoluene itself with irradiation of uv light as a first step of the investigation of deterioration of plastic scintillators.

§2. Experimental

Sample preparation. Two kinds of samples were prepared. One contains anthracene with the concentration of 1 g/l. The other does not contain any other additive materials. They were prepared by thermal polymerization.[14] The sample number and their corresponding polymerization conditions are listed in Table I.

The large part of this experiment was done with bulk and film samples. For absorption measurements, solution or film samples were

Table I. Sample number and corresponding polymerization conditions.

Sample number	Polymerization temperature (°C)	Polymerization time (h)	Additive solute
P-95-680	95	680	—
P-150-35	150	35	—
P-200-25	200	25	—
P-200-10	200	10	—
P-200-5	200	5	—
A-95-680	95	680	anthracene
A-150-35	150	35	anthracene
A-200-25	200	25	anthracene
A-200-10	200	10	anthracene
A-200-5	200	5	anthracene

used. In the case of bulk samples various surface treatments were tried. (a) "fresh surface": cut off an old surface layer just before irradiation or fluorescence measurements. (b) "polished surface": polish the surface with sandpaper while pouring cold water and then with a filter paper. (c) "xylene-polished" or "monomer-polished surface": polish the surface with a filter paper which is soaked with some solvent, xylene or vinyltoluene monomer. Polished and solvent polished surfaces are very clear and transparent but fresh surfaces are opaque.

Film samples were prepared by the following procedures. One gram of polymer was dissolved in about 100 ml of benzene. About 50 ml of the solution was slowly poured into about 500 ml of ethanol that was vigorously stirred. Precipitated polymer was gathered on a filter paper and then the solvents were eliminated by evaporation. It may be considered that most of the residual vinyltoluene monomer in the sample was removed in these processes. This refined polymer was dissolved again in cyclohexane and a proper volume of the solution was poured on a slide glass and then the solvent was removed by evaporation. The rate of evaporation of solvent cyclohexane was controlled so as to obtain a film with a clear and nonwrinkled surface. The films obtained in the above manner are to be called "monomer-free film" hereafter. When the film sample containing vinyltoluene monomer was desired, a known amount of the monomer was added to the cyclohexane solution. Then, from this solution films were prepared in the same manner described above. The concentration of the monomer remaining in the film was determined by absorption measurement of the film just before it was used.

Irradiation, fluorescence and absorption. For fluorescence measurements, three geometrical arrangements are usually used[15]: right angle method, frontal method and in-line method. In polyvinyltoluene-anthracene system, polyvinyltoluene strongly absorbs the light with the wavelength shorter than about 300 mμ and the fluorescence of the polymer is absorbed by anthracene. When the in-line method was used, the polymer fluorescence could not be detected for the thick samples. Therefore, the frontal method was used in this study. A 150 W Xe arc lamp (USHIO 150–DS) was used for the irradiation and fluorescence excitation light source. The monochromatized light from the lamp was focussed on the surface of the sample. Though the absolute value of irradiation dose was not measured, irradiation intensity was monitored. Irradiation dose of one unit used in this paper corresponds to the irradiation for about 1.6 minutes in our experimental apparatus. The irradiated area was about 25 mm^2. The fluorescence light was observed through an analyzing monochromator by a Hamamatu TV R–106 photomultiplier. The absorption and fluorescence of the samples were recorded with use of Hitachi-Perkin-Elmer electrophotometer. The fluorescence spectra obtained were not corrected for the spectral response of the photomultiplier and the analyzing monochromator.

§3. Results and Discussion

3.1 *Fluorescence of vinyltoluene monomer and polymer*

Fluorescence spectra of monomer-free or monomer-containing polyvinyltolune and of vinyltoluene monomer are shown in Fig. 1 for various sample forms. The excitation wavelength was 260 mμ in all cases and that wavelength lies in the first electronic excitation band of the phenylic segmer of the samples. The frontal excitation method was used for solid samples and the right-angle method for solution samples. Vinyltoluene monomer was found to be very fluorescent at low concentrations. In cyclohexane solution, the fluorescence intensity of the monomer becomes maximum at the concentration of about 3×10^{-4} M/l and it decreases at higher concentrations. As seen in Fig. 1, the monomer-containing sample has its maximum peak at about 312 mμ and a small peak or shoulder at about 300 mμ. Comparison of the fluorescence spectra of (b)-(d) with that of (a) suggests that the fluorescence from polyvinyltoluene which is polymerized thermally in the usual manner may be attributed to the residual monomer. On the other hand, for monomer-free samples the fluorescence spectra differ from those of monomer-containing samples in the following points: they have no fluorescence peak at 312 mμ but have a broad and structureless band at about 330 mμ. In cyclohexane solution, they have an appreciable

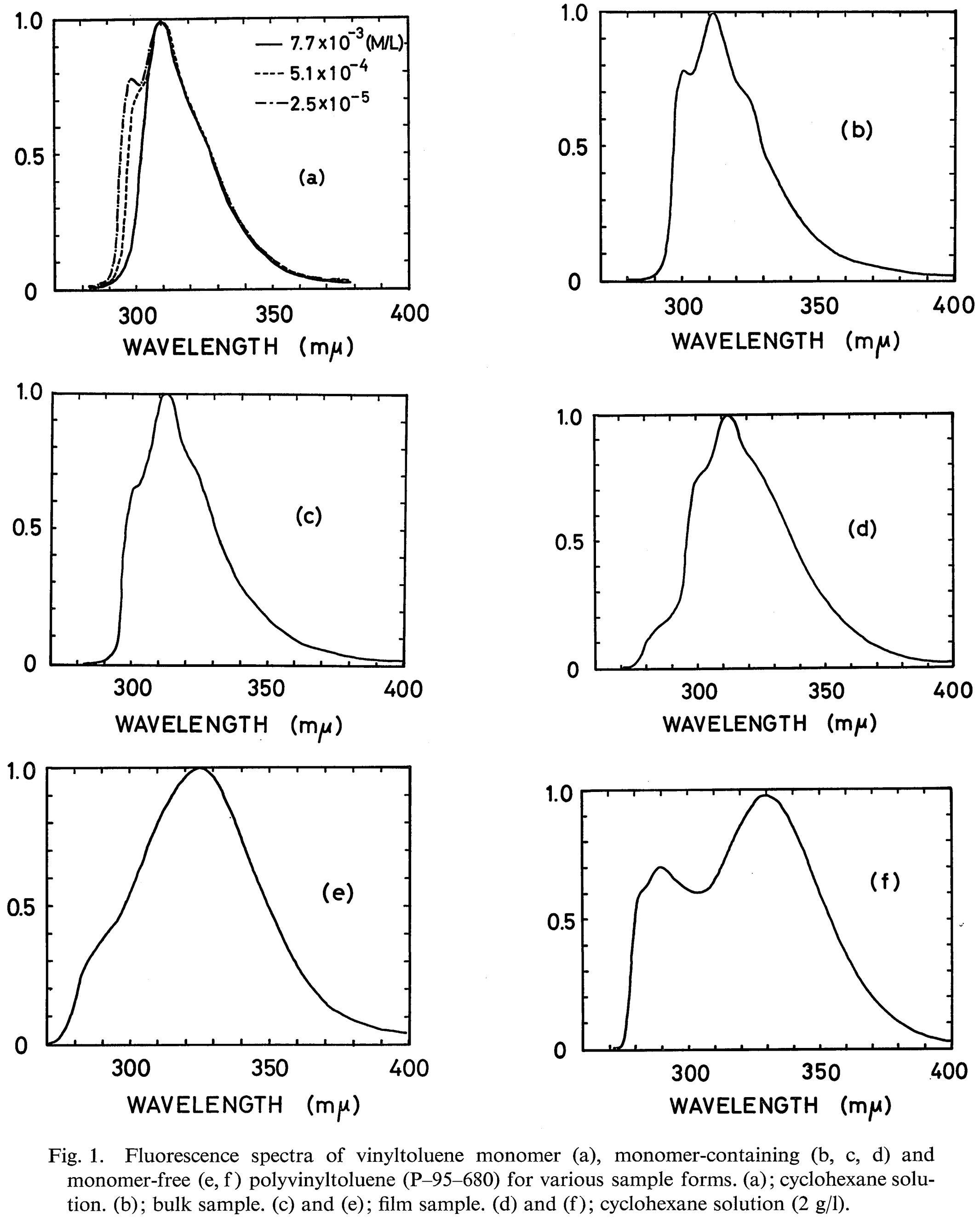

Fig. 1. Fluorescence spectra of vinyltoluene monomer (a), monomer-containing (b, c, d) and monomer-free (e, f) polyvinyltoluene (P–95–680) for various sample forms. (a); cyclohexane solution. (b); bulk sample. (c) and (e); film sample. (d) and (f); cyclohexane solution (2 g/l).

band around 280–290 mμ. For monomer-containing samples, however, we could not observe any band corresponding to the above 280–290 mμ band except for a small peak or shoulder in the solution samples. The effect of the residual styrene monomer on the fluorescence spectra of plastic scintillators with polystyrene base has been reported in detail by Basile.[16,17]

In our samples the excited segmer of polyvinyltoluene falls to the ground state to release its excitation energy as different fluorescence in the following three competitive processes: (1) it may fall to the ground state directly to emit the fluorescence at 280–290 mμ that is called normal fluorescence or segmer fluorescence. (2) it may transfer the excitation energy to the residual monomer. The excited monomer then emits its characteristic fluorescence with a main peak at 312 mμ and a small peak or shoulder at 300 mμ. These 312 and 300 mμ peaks correspond to the 298 and 310 mμ peaks of the monomer in cyclohexane solutions, respectively. Because of reabsorption effect, the intensity of the 300 mμ peak depends on the monomer concentration and it may become a shoulder at higher concentrations (see Fig. 1(a)). (3) when the segmers in excimer state dissociate, a broad structureless fluorescence appears.$^{18)}$ For polystyrene, this excimer fluorescence appears at about 330 mμ.$^{19,20)}$ In our polyvinyltoluene system, the broad fluorescence bands with a maximum peak at about 325 mμ (for solid sample) or 330 mμ (for solution sample) may be attributed to this excimer fluorescence.

For the samples containing anthracene, the fluorescence spectra were practically the same as those of the samples of pure polyvinyltoluene with the exception of having the characteristic fluorescence band of anthracene in the longer wavelength region.

3.2 *Fluorescence degradation*

Irradiation of the samples with uv light causes reduction of the fluorescence intensity. This degradation of fluorescence was studied by observing the fluorescence intensity at the maximum peak of the fluorescence spectrum. Irradiation was made at 260 mμ for all samples.

Surface treatment effect. It has been reported that the fluorescence spectrum of polystyrene is markedly dependent on the excitation wavelength.$^{21,22)}$ This effect is attributed to morphological differences of the different surface layers. Different surface states may cause different fluorescence properties such as fluorescence spectrum and fluorescence degradation. The effect of surface state was examined with the various surface treatments in our samples. The fluorescence spectrum of our samples was not affected in its essential features by our four surface treatments (fresh surface, polished surface, xylene-polished surface and monomer-polished surface). As for fluorescence degradation, however, it is markedly dependent on the surface treatments. The sample with monomer-polished surface especially displays quite different behavior from the samples with the other three surface treatments. With monomer-polished surface, the fluorescence intensity increases rapidly with irradiation and reaches a value of its saturation. Then, it gradually decreases in the same way as the other surface treatment samples. An initial value of the fluorescence intensity is very small for the sample with monomer-polished surface. This singular behavior of monomer-polished surface suggests that the reduction of the fluorescence intensity by irradiation of uv light is affected very much by the monomer remaining in the samples. The other three surface treatments produced almost the same fluorescence degradation, but the reproducibility is poor for the samples with the polished-surface or xylene-polished surface. For the sample with the fresh surface, the reproducibility is fairly good. The poor reproducibility of the samples with the polished surface or xylene-polished surface is thought to be caused by alteration of the local monomer concentration in the surface layer of the samples during the process of surface treatment. Therefore, only the fresh surface treatment was used in all cases of bulk samples.

Ambient gas effect. Oxygen effect of fluorescence degradation of polymers is well expected but the effect has not been reported. Usually, irradiations were made only in air for polymer systems$^{2-5,11-13)}$ and for anthracene crystals.$^{1,6-10)}$

The fluorescence degradation was examined in oxygen, nitrogen, argon and air ambient gases. The degradation curves are shown in Fig. 2 for the sample of P–95–680. As was expected it is definitely concluded that oxygen enhances the fluorescence degradation. In nitrogen and argon gases, the degradation curves are indistiguishable within experimental error.

Effect of the residual monomer. Our preliminaly experiment for the samples with the monomer-polished surface suggests that the residual monomer may play an important role in the fluorescence degradation. In order to study the effect of the monomer, fluorescence degradation was examined for the various samples which were prepared at different polymerization conditions. Several curves of fluorescence degradation are shown in Fig. 3 for various samples. Figure 3(a) is for the samples of pure polyvinyltoluene and Fig. 3(b) is for the samples containing anthracene. These

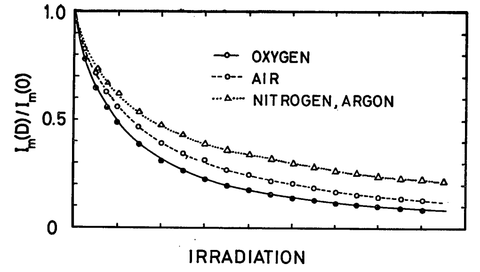

Fig. 2. Degradation curves of monomer-containing sample (P–95–680) in various ambient gases.

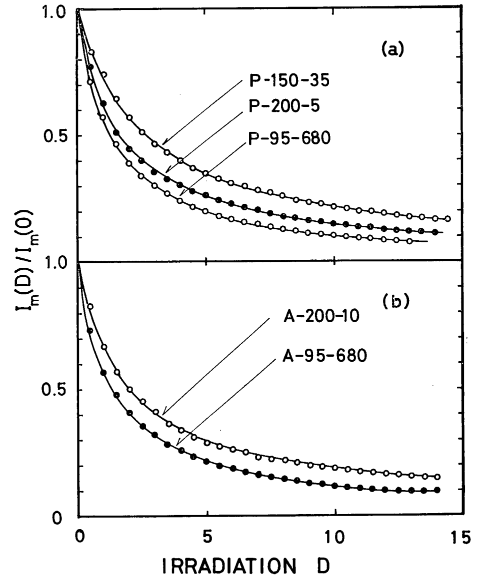

Fig. 3. Degradation curves of monomer-containing samples of pure polyvinyltoluene (a) and of anthracene doped polyvinyltoluene (b).

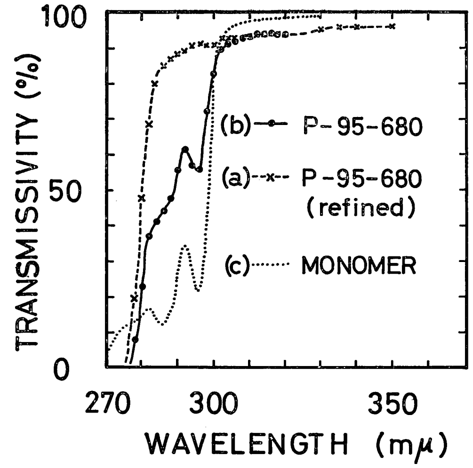

Fig. 4. Transmission spectra of monomer-free (a) and monomer-containing (b) polyvinyltoluene, and of vinyltoluene monomer (c). (a) and (b); cyclohexane solution of 2 g/l. (c); cyclohexane solution of 7.7×10^{-3} M/l.

fluorescence degradation curves were all recorded by observing the fluorescence intensity at the maximum peak of their fluorescence. Irradiation was made in air for all samples. The concentration of the monomer remaining in the samples was determined by absorption measurement. The typical absorption spectra of cyclohexane solutions of the monomer, monomer-free and monomer-containing samples of P–95–680 are shown in Fig. 4. With comparison of these absorption spectra, the concentration of the monomer can be evaluated with the assumption that the difference of the optical density at 296 mμ between (a) and (b) in Fig. 4 is due to the residual monomer.

3.3 *Mechanism of fluorescence degradation*

Form of degradation curve. Fluorescence degradation may be caused by the following three processes.

(1) Direct damage. Irradiation of uv light destroys the fluorescent molecules and changes them to non-fluorescent.

(2) Filter effect. Absorption centers which are produced by irradiation reduce the fluorescence yield due to "inner filter effect."

(3) Quenching. Excited molecules of the sample are deactivated with a high efficiency by quenching centers which are produced by irradiation. In quenching, there are two possible cases. One is solvent quenching. In this case excited polymer segments are quenched. The other is solute quenching. In this case the excitation energy is transferred from the polymer segments to the residual monomer molecules. Then, the excited monomer molecules are quenched.

Taking the above three processes into account, mechanism of the fluorescence degradation is considered. In our samples, most of the exciting light is absorbed by phenylic segmers of polyvinyltoluene, and then the excitation energy is dissipated by several processes: emission of polymer fluorescence, transfer of the excitation energy to the residual monomer and to the quenching centers which are produced by irradiation, and forming the excimer state. A scheme for emission, energy transfer, quenching and excimer forming is

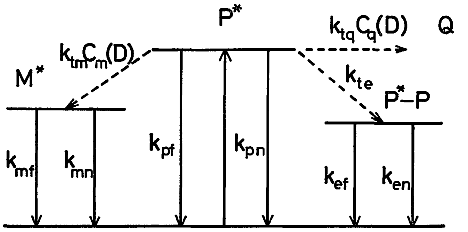

Fig. 5. A scheme for emission, energy transfer, quenching and excimer forming. P*, M*, P*–P and Q represent excited state of polymer segment, excited state of monomer, excimer state of polymer and quencher.

depicted by Fig. 5 in the case of solvent quenching. The k's specified with suffixes represent the following rate constants.

k_{pf}, k_{mf}, k_{ef}: rates of fluorescent decay of excited polymer segments, excited monomer molecules and excimers, respectively.

k_{pn}, k_{mn}, k_{en}: rates of internal quenching of excited polymer segments, excited monomer molecules and excimers, respectively.

k_{te}: rate of formation of excimer.

$k_{tm} \cdot C_m(D)$: rate of energy transfer from excited polymer segments to monomer molecules.

$k_{tq} \cdot C_q(D)$: rate of quenching of excited polymer segments by quenching centers.

$C_m(D)$, $C_p(D)$: monomer and polymer concentrations at the irradiation dose D.

$C_q(D)$: concentration of quenching centers produced by the irradiation dose D.

$F_m(D)$, $F_p(D)$, $F_e(D)$: coefficients of filter effect for monomer fluorescence, normal fluorescence and excimer fluorescence, respectively.

They are normalized in such a way that $F_m(0)$, $F_p(0)$ and $F_e(0)$ are unity. From the above scheme, monomer fluorescence $I_m(D)$, normal (or segmer) fluorescence $I_p(D)$ and excimer fluorescence $I_e(D)$ are given by the following equations, respectively.

$$I_m(D)=A_m \cdot \frac{k_{tm} \cdot C_m(D)}{k_{pf}+k_{pn}+k_{te}+k_{tq} \cdot C_q(D)+k_{tm} \cdot C_m(D)} \cdot \frac{k_{mf}}{k_{mf}+k_{mn}} \cdot F_m(D) \tag{1}$$

$$I_p(D)=A_p \cdot \frac{k_{pf}}{k_{pf}+k_{pn}+k_{te}+k_{tq} \cdot C_q(D)+k_{tm} \cdot C_m(D)} \cdot F_p(D) \tag{2}$$

$$I_e(D)=A_e \cdot \frac{k_{te}}{k_{pf}+k_{pn}+k_{te}+k_{tq} \cdot C_q(D)+k_{tm} \cdot C_m(D)} \cdot \frac{k_{ef}}{k_{ef}+k_{en}} \cdot F_e(D) \tag{3}$$

where A_m, A_p and A_e are proportional constants.

Our experiments show that normal fluorescence $I_p(D)$ is negligiblly small in our solid samples and a small amount of the residual monomer gives rise to drastic suppression of the excimer fluorescence.

Irradiation of polymers such as polystyrene by uv light causes photochemical reactions. Recently Aoki et al proposed a reaction scheme which leads to chain scission and mechanical deterioration of polystyrene.[23] Such photochemical reactions may be caused in our polyvinyltoluene samples. In this paper we call for convenience the photochemical products in our samples absorption or quenching center, though we can not know at the present stage their chemical structures and which of these photochemical products acts the absorption center or the quenching center. As for the absorption center, we can experimentally estimate its practical effect on the fluorescence degradation. On the contrary, the concentration of the quenching center can not be evaluated experimentally.

Provided that monomer concentration $C_m(D)$ and polymer concentration $C_p(D)$ decrease by uv irradiation in accordance with the following equations,

$$-\frac{\mathrm{d}C_m(D)}{\mathrm{d}D}=k_m \cdot C_m(D) \tag{4}$$

$$-\frac{\mathrm{d}C_p(D)}{\mathrm{d}D}=k_p \cdot C_p(D) \tag{5}$$

then, for small irradiation, $C_m(D)$ and $C_p(D)$ are expressed as

$$\begin{aligned} C_m(D) &= C_m(0) \cdot \exp(-k_m \cdot D) \\ &\simeq C_m(0) \cdot (1-k_m \cdot D) \end{aligned} \tag{6}$$

$$C_p(D) = C_p(0) \cdot \exp(-k_p \cdot D) \simeq C_p(0) \cdot (1 - k_p \cdot D) \qquad (7)$$

where k_m and k_p are proportional constants.

It is plausible to assume that the concentration of the quenching center is proportional to the amount of the photochemical products. Therefore, for small irradiation the concentration of the quenching center $C_q(D)$ is obtained with use of eqs. (6) and (7).

$$\begin{aligned} C_q(D) &= k'_{qm} \cdot [C_m(0) - C_m(D)] \\ &\quad + k'_{qp} \cdot [C_p(0) - C_p(D)] \\ &\simeq [k_{qm} \cdot C_m(0) + k_{qp} \cdot C_p(0)] \cdot D \qquad (8) \end{aligned}$$

where k'_{qm}, k'_{qp}, k_{qm} and k_{qp} are proportional constants. In eq. (8), assumption is made for convenience that quenching centers which are produced from the monomer and the polymer are the same. The value of $C_p(0)$ can be approximately taken as unity.

For small irradiation such that $k_m \cdot D \ll 1$, from eqs. (1), (6) and (8) initial monomer fluorescence $I_m(0)$ and degradation curve $I_m(D)/I_m(0)$ are obtained.

$$I_m(0) = A_m \cdot \frac{\alpha \cdot C_m(0)}{1 + \alpha \cdot C_m(0)} \cdot \beta \qquad (9)$$

$$\alpha = \frac{k_{tm}}{k_{pf} + k_{pn} + k_{te}}$$

$$\beta = \frac{k_{mf}}{k_{mf} + k_{mn}} \cdot F_m(0) = \frac{k_{mf}}{k_{mf} + k_{mn}}$$

$$\frac{I_m(D)}{I_m(0)} = \frac{1}{1 + K_m \cdot D} \cdot F_m(D) \qquad (10)$$

$$K_m = \frac{k_{tq} \cdot [k_{qm} \cdot C_m(0) + k_{qp}]}{k_{pf} + k_{pn} + k_{te} + k_{tm} \cdot C_m(0)}$$

here, K_m is a degradation constant. If the filter effect is negligibly small ($F_m(D) \simeq 1$), then eq. (10) becomes a Stern-Volmer type equation,

$$\frac{I_m(D)}{I_m(0)} = \frac{1}{1 + K_m \cdot D} \qquad (11)$$

From eq. (11), one can obtain $D_{1/5}$ that is defined as an irradiation dose which causes the reduction of the fluorescence intensity to 1/5 of the initial value $I_m(0)$.

$$D_{1/5} = \frac{\gamma + \delta \cdot C_m(0)}{1 + \xi \cdot C_m(0)} \qquad (12)$$

$$\gamma = 4 \cdot \frac{k_{pf} + k_{pn} + k_{te}}{k_{tq} \cdot k_{qp}}$$

$$\delta = 4 \cdot \frac{k_{tm}}{k_{tq} \cdot k_{qp}}$$

$$\xi = \frac{k_{qm}}{k_{qp}}$$

Since a trace of the residual monomer suppresses the excimer fluorescence, the excimer fluorescence can be observed only when $C_m(0) \simeq 0$. Then, for $F_e(D) \simeq 1$, the Stern-Volmer type equation is derived from eq. (3) for excimer fluorescence too.

$$\frac{I_e(D)}{I_e(0)} = \frac{1}{1 + K_e \cdot (D)} \qquad (13)$$

$$K_e = \frac{k_{tq} \cdot k_{qp}}{k_{pf} + k_{pn} + k_{te}}$$

For excimer fluorescence, $D_{1/5}$ is given by

$$D_{1/5} = 4 \cdot \frac{k_{pf} + k_{pn} + k_{te}}{k_{tq} \cdot k_{qp}} \qquad (14)$$

Equations (13) and (14) are found to be identical with eqs. (11) and (12) respectively, putting $C_m(0) = 0$ in these equations.

In the case of solute quenching, $I_m(0)$ and $I_m(D)/I_m(0)$ are expressed in the same equations as those for solvent quenching. For the expression of $D_{1/5}$, slight alterations of

$$\delta = 0, \quad \text{and} \quad \gamma = 4 \cdot (k_{mf} + k_{mn})/k_{tq} \cdot k_{qp}$$

are required.

Equations (9) and (12) represent a relation between the initial fluorescence intensity $I_m(0)$ and the initial monomer concentration $C_m(0)$ and that between $D_{1/5}$ and $C_m(0)$, respectively. If the fluorescence degradation obeys eq. (11) in our samples, a plot of $I_m(0)/I_m(D) - 1$ against D will give a straight line of slope K_m. In Fig. 6, plots of $I_m(0)/I_m(D) - 1$ against D are represented for pure polyvinyltoluene bulk samples, anthracene doped bulk samples and pure polyvinyltoluene film samples. Figures 7 and 8 show the relation between initial concentration of the monomer $C_m(0)$ and the initial monomer fluorescence $I_m(0)$ and that between $C_m(0)$ and $D_{1/5}$, respectively. In Fig. 7, a calculated curve is also represented for $\alpha = 1.0 \times 10^2$, $A_m \cdot \beta = 1.4 \times 10$ in eq. (9). This large value of α suggests that the transfer efficiency of the excitation energy from polyvinyltoluene to the monomer is very high and monomer fluorescence is dominant. This suggestion agrees with our experimental fact that a slight amount of

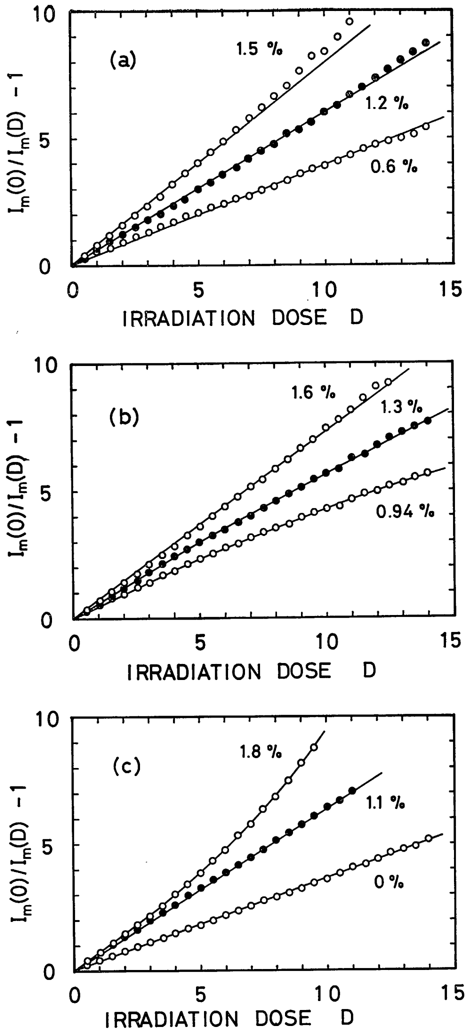

Fig. 6. $I_m(0)/I_m(D)-1$ versus D for the bulk samples of pure polyvinyltoluene (a), anthracene doped polyvinyltoluene (b) and for the film samples of pure polyvinyltoluene (c). Concentration of the monomer are given in the figures.

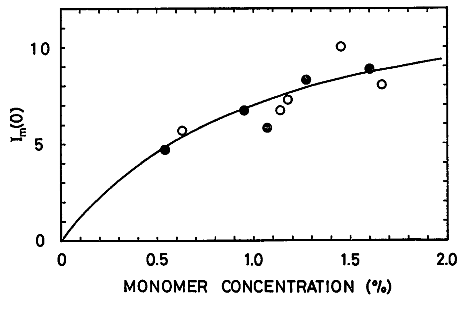

Fig. 7. $I_m(0)$ versus initial monomer concentration $C_m(0)$. ○ ; bulk samples of pure polyvinyltoluene. ● ; bulk samples of anthracene doped polyvinyltoluene.

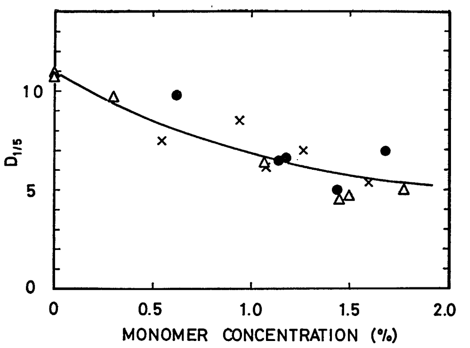

Fig. 8. $D_{1/5}$ versus initial monomer concentration $C_m(0)$. ● ; bulk samples of pure polyvinyltoluene. × ; bulk samples of anthracene doped polyvinyltoluene. △ ; film samples of pure polyvinyltoluene.

the monomer induces monomer fluorescence with suppression of normal fluorescence or excimer fluorescence. With the use of eq. (12) qualitative relation between $D_{1/5}$ and $C_m(0)$ may be discussed. The value of the term $\delta\cdot C_m(0)$ in eq. (12) is roughly estimated. Since the maximum concentration of the residual monomer is about 2% in our experiment, the numerical value of $C_m(0)$ is less than 2×10^{-2}. The numerical value of γ is obtained experimentally to be 11 from the observed value of $D_{1/5}$ with the monomer-free sample. With use of these numerical values,

$$\frac{\delta\cdot C_m(0)}{\gamma}=\frac{4\cdot\xi\cdot C_m(0)}{\gamma}\cdot\frac{k_{tm}\cdot C_m(0)}{k_{tq}\cdot k_{qm}\cdot C_m(0)}$$

$$<10^{-2}\cdot\xi\cdot\frac{k_{tm}\cdot C_m(0)}{k_{tq}\cdot k_{qm}\cdot C_m(0)}$$

In the above expression, the term $k_{tm}\cdot C_m(0)$ is the energy transfer rate from excited polymer segments to the residual monomer and the term $k_{tq}\cdot k_{qm}\cdot C_m(0)$ is that from excited polymer segments to the quenching centers which are produced from the monomer by the irradiation of unit dose. In solvent quenching, rate of energy transfer from the excited polymer segments to the residual monomer is smaller than that from the excited polymer segments to the quenching centers. Therefore, it is reasonable to expect that $k_{tm}\cdot C_m(0)\lesssim k_{tq}\cdot k_{qm}\cdot C_m(0)$ If ξ is not so much large, the term $\delta\cdot C_m(0)$ may be neglected in comparison with γ. From the definitions of δ and γ, the ratio of $\delta\cdot C_m(0)$ and γ is rewritten in another form.

$$\frac{\delta\cdot C_m(0)}{\gamma}=\frac{k_{tm}\cdot C_m(0)}{k_{pf}+k_{pn}+k_{te}}$$

When we can assume that the fluorescence quantum yield of polyvinyltoluene is not so different from that of polystyrene and that $k_{tm} \cdot C_m(0)$ is not so large, inequality of $k_{pf}+k_{pn}+k_{te}>k_{tm} \cdot C_m(0)$ may be expected even when $k_{pf}+k_{te}<k_{tm} \cdot C_m(0)$ because of the low fluorescence quantum yield of 0.03.[24] Therefore, the ratio becomes small and the term $\delta \cdot C_m(0)$ is neglected. When $k_{tm} \cdot C_m(0)$ is very large, the assumption of solvent quenching breaks and it turns to be solute quenching. In this case the term δ vanishes. In any case, though the physical meaning of γ is somewhat different in the two cases, $D_{1/5}$ is expected to vary practically with the residual monomer concentration in the form of

$$D_{1/5}=\frac{\gamma}{1+\xi \cdot C_m(0)}$$

In other words, from eq. (12) we can not determine experimentally which is the more acceptable case. A calculated curve of eq. (12) for $\gamma=11$, $\delta \cdot C_m(0)=0$ and $\xi=6\times 10$ is also represented in Fig. 8. A large value of ξ (6×10) means that the monomer is more easily changed to quenchers than the polymer. This fact may arise from their difference in chemical stability.

As is seen from Figs. 7 and 8, a fairly good agreement of the calculated curves of eqs. (9) and (12) to their corresponding experimental deta and linear relationship between $I_m(0)/I_m(D)-1$ and D in Fig. 6 lead to a conclusion that the fluorescence degradation of our samples is affected very much by the residual monomer and is well described by eqs. (11) and (13) for small irradiation doses for monomer and excimer fluorescence, respectively.

Here, some discussions are made from the viewpoint of energy-transfer mechanism whether solvent quenching or solute quenching is more acceptable. In the case of solute quenching, three possibilities are considered in the energy-transfer mechanism[25] between the residual monomer or excimer to the quencher: Förster mechanism, Stern-Volmer mechanism and active sphere model. The Stern-Volmer mechanism must be discarded for the following reason, though the observed fluorescence degradation obeys the Stern-Volmer type equation. In this mechanism there must be excitation migration. The possibility of excitation migration can be neglected, since there is small probability of finding many monomer molecules or excimer-forming sites next to each other. In the active sphere model the degradation curve must be exponential. Our observation of non-exponential degradation eliminates this possibility. In the Förster mechanism, the degradation curve obeys the following equation,[25]

$$\frac{I_m(D)}{I_m(0)}=1-\pi^{1/2} \cdot \eta \cdot \exp \eta^2 \cdot (1-\operatorname{erf} \eta) \quad (15)$$

where η is a quantity being proportional to the quencher concentration and erf η is the error function. If $\eta \ll 1$, the value of $I_m(0)/I_m(D)-1$ increases linearly with η and this leads to a confusing Stern-Volmer type equation. Therefore, it is essential that the observation must be taken over a wide range of the quencher concentration. In our experiments the absolute value of the quencher concentration cannot be estimated but we can evaluate the value of η from eq. (15) with use of the observed value of $I_m(D)/I_m(0)$. For example, for $I_m(D)/I_m(0)$ is 1/7, η is 1.5 and this violates the assumption of $\eta \ll 1$. The value of $I_m(0)/I_m(D)-1$ should increase greater than linearly. Instead, the Stern-Volmer relation holds fairly well in this region as is seen in Fig. 6. Thus the Förster mechanism is also eliminated. Therefore, from these considerations solvent quenching is more acceptable.

According to the recent work of Powell,[26] exciton migration occurs in polyvinyltoluene and excimer-forming sites and the short-wavelength fluor such as *p*-terphenyl act as exciton traps.

After all, from the above considerations, it is thought to be a correct picture in our sample that excitation energy of the phenylic segmer of polyvinyltoluene migrates as excitons in the sample and is trapped by the residual monomer molecules, excimer-forming sites and the quenching centers which are produced by uv irradiation.

Direct damage. In order to estimate a decrease of the monomer concentration by irradiation, optical densities of monomer-containing and monomer-free samples are measured for various irradiation doses. They are presented in Figs. 9 and 10. Figure 9 is for the monomer-containing sample (1.45 %) and Fig. 10 is for the monomer-free sample. As is seen from Figs. 9 and 10,

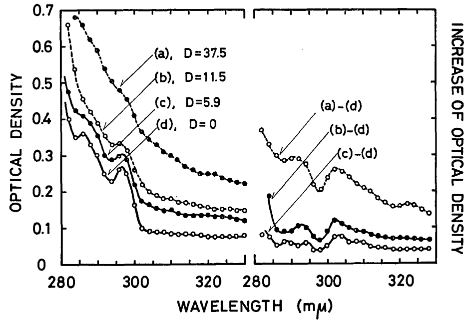

Fig. 9. Absorption spectra of monomer-containing film sample of pure polyvinyltoluene (P–95–680) at various irradiation doses. monomer concentration; 1.45%. film thickness; 1.54 mg/cm².

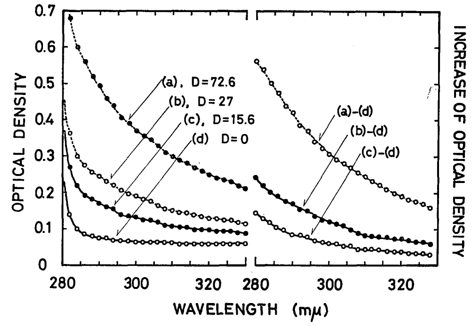

Fig. 10. Absorption spectra of monomer-free film sample of pure polyvinyltoluene (P–95–680) at various irradiation doses. film thickness; 1.0 mg/cm².

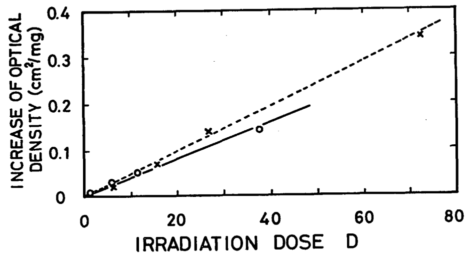

Fig. 11. Increase of absorption coefficient at 296 mμ for monomer-free (--×--) and monomer-containing (—○—) film samples of pure polyvinyltoluene (P–95–680).

appreciable changes are found in the optical densities between monomer-free and monomer-containing samples in the wavelength region of the characteristic absorption band of the monomer. From Figs. 9 and 10, increases of the absorption coefficient which are produced at 296 mμ are calculated for the monomer-containing sample (1.54 mg/cm² in thickness) and the monomer-free sample (1.0 mg/cm² in thickness). They are presented in Fig. 11. If the difference in the increase of the absorption coefficient for both samples is due to decrease of the monomer concentration $C_m(D)$, $C_m(D)$ is expressed as

$$C_m(D) = C_m(0) \cdot (1 - 1 \times 10^{-2} \cdot D) \qquad (16)$$

Equation (16) agrees well with eq. (6) and for small irradiation doses the condition of $k_m \cdot D \ll 1$ is fulfilled.

If the monomer fluorescence intensity is proportional to the monomer concentration, the fluorescence intensity decreases proportionally to $f_m(D) = C_m(D)/C_m(0)$. For the monomer-containing sample (about 1.5%), $f_m(D)$ is obtained from eq. (16),

$$f_m(D) = 1 - 1 \times 10^{-2} \cdot D \qquad (17)$$

and reduction of the fluorescence intensity is 5~6% at most for the irradiation does of $D_{1/5}$ because the experimental value of $D_{1/5}$ for this sample is 5~6. However, it is obvious from the definition of $D_{1/5}$ that the irradiation of $D_{1/5}$ reduces the fluorescence intensity by 80% of the original value. Therefore, decrease of the monomer is too small to explain the whole observed fluorescence degradation. This conclusion is also supported by the fluorescence spectra which were observed at various irradiation doses. They are shown in Fig. 12. As is seen in Fig. 12, characteristic monomer features are found in the fluorescence spectra until the fluorescence intensity becomes very small.

Filter effect. As was mentioned before, the

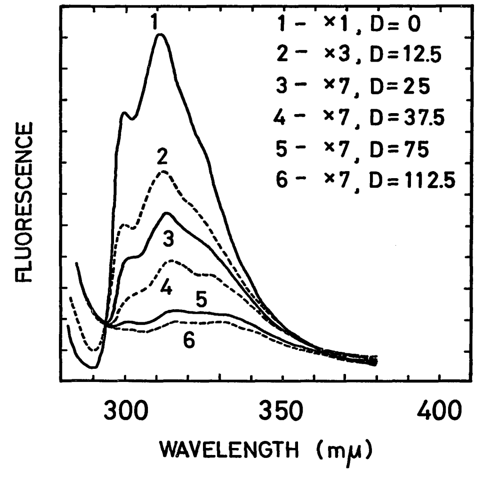

Fig. 12. Fluorescence spectra of monomer-containing bulk samples of anthracene doped polyvinyltoluene (A–95–680) for various irradiation doses.

absorption centers which are produced by irradiation have a filter effect. This filter effect is roughly estimated below.

Since the effective excitation energy ΔI_{eff} that is absorbed in a thin layer between x and $x+\mathrm{d}x$ in Fig. 13 is expressed as

$$\Delta I_{\mathrm{eff}} = \frac{d_e(0)}{d_e(D)} \cdot [I(x) - I(x+\mathrm{d}x)]$$

$$= I_0 \frac{d_e(0)}{l} \cdot \ln 10 \cdot 10^{-d_e(D)\cdot x/l} \mathrm{d}x \quad (18)$$

observable fluorescence from this thin layer through the residual layer of the sample is given by the following equations.

$$\Delta L_f(D) = q \cdot \Delta I_{\mathrm{eff}} \cdot 10^{-d_f(D)\cdot x/l} \quad (19)$$

$$\Delta L_r(D) = q \cdot \Delta I_{\mathrm{eff}} \cdot 10^{-d_f(D)\cdot(l-x)/l} \quad (20)$$

$\Delta L_f(D)$, $\Delta L_r(D)$: observable fluorescence intensities from the frontal and rear surface, respectively.

$d_e(0)$, $d_e(D)$: optical densities at excitation wavelength before and after irradiation.

$d_f(D)$: optical density in the wavelength region of the fluorescence after irratiation.

q: fluorescence quantum efficiency.

l: sample thickness.

I_0, $I(x)$, $I(x+\mathrm{d}x)$: exciting light intensities at the surface, x and $x+\mathrm{d}x$, respectively.

If $d_e(D) \gg d_f(D)$, as is the case, the observable frontal and rear fluorescence intensities $L_f(D)$ and $L_r(D)$ are obtained from eqs. (18), (19) and (20).

$$L_f(D) = q \cdot I_0 \cdot \frac{d_e(0)}{d_e(D)} \cdot [1 - 10^{-d_e(D)}] \quad (21)$$

$$L_r(D) = q \cdot I_0 \cdot \frac{d_e(0)}{d_e(D)} \cdot [1 - 10^{-d_e(D)}] \cdot 10^{-d_f(D)} \quad (22)$$

As is seen in eqs. (21) and (22), in the case of the frontal excitation, the absorption band in the region of fluorescence does not play as a filter. This agrees with the fact that the reabsorption effect is less serious in the case of the frontal excitation. From eqs. (21) and (22), coefficients of the filter effect $F_f(D)$ and $F_r(D)$ are defined in both cases.

$$F_f(D) = \frac{L_f(D)}{L_f(0)} = \frac{d_e(0)}{d_e(D)} \cdot \frac{1-10^{-d_e(D)}}{1-10^{-d_e(0)}} \quad (23)$$

$$F_r(D) = \frac{L_r(D)}{L_r(0)} = \frac{d_e(0)}{d_e(D)} \cdot \frac{1-10^{-d_e(D)}}{1-10^{-d_e(0)}} \cdot 10^{-(d_f(D)-d_f(0))} \quad (24)$$

In the above derivation, uniform distribution of the absorption centers in the sample is assumed. Values of $F_f(D)$ and $F_r(D)$ are estimated by observing the optical densities in the wavelength regions of excitation and fluorescence at various irradiations. In the wavelength region of excitation, the absorption coefficient is so high that a very thin film sample must be used. Therefore, the monomer concentration cannot be determined in this thin film. We used the monomer-free film that was prepared from the refined polymer. The absorption spectra in this region are presented in Fig. 14 at various irradiations. Figure 15 shows the relation between optical densities and irradiation dose in this region. In the wavelength region of fluorescence, increases of optical densities are measured at 312 and 325 mμ for monomer fluorescence and excimer fluorescence, respectively. They are shown in Fig. 16. From these experimental deta,$F_f(D)$ and $F_r(D)$ are obtained with use of eqs. (23) and (24). It is important to note that the value of $d_e(D)$ is obtained with use of the very thin monomer-free film (it is thinner than the penetration depth of the irradiation

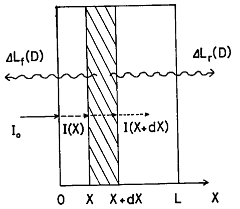

Fig. 13. Illustration for derivation of coefficients of filter effect.

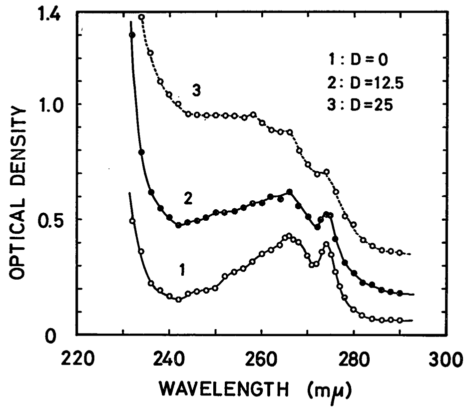

Fig. 14. Absorption spectra of monomer-free film sample of pure polyvinyltoluene (P–95–680).

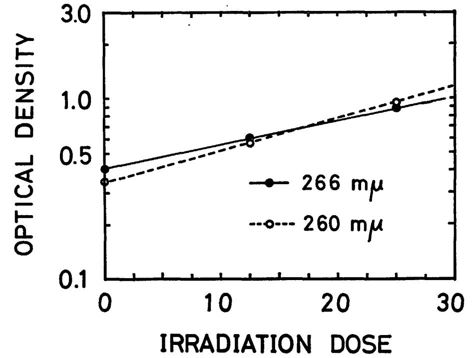

Fig. 15. Optical density versus D for monomer-free film sample of pure polyvinyltoluene (P–95–680).

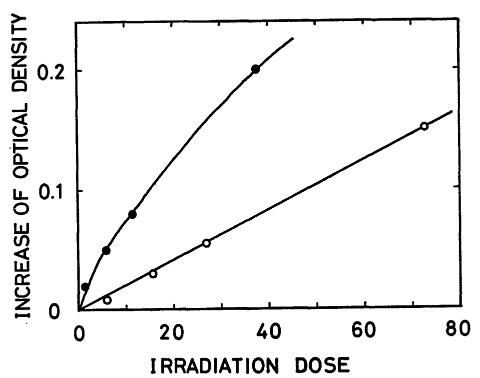

Fig. 16. Increase of optical density of pure polyvinyltoluene (P–95–680) in the region of fluorescence. ○; monomer-free film. film thickness; 1.0 mg/cm^2. ●; monomer-containing film. film thickness; 1.54 mg/cm^2. monomer concentration; 1.45%.

light). Therefore, this value is over-estimated and, rigorously speaking, the value cannot be applied to the case of monomer-containing samples. In Fig. 17, $F_f(D)$, $F_r(D)$, $f_m(D)$, $f_m(D)\cdot F_f(D)$, $f_m(D)\cdot F_r(D)$ and the experimentally observed degradation curve for the monomer-containing samples (1.5%, 1.54 mg/cm^2) are shown. Since the frontal excitation method is used in our experiments, $F_m(D)$ and $F_e(D)$ become to $F_f(D)$, and apparent fluorescence degradation arising from the decrease of the monomer concentration and the filter effect is expected as $f_m(D)\cdot F_f(D)$ and $F_f(D)$ for our monomer-containing and monomer-free samples, respectively. For the monomer-containing sample (1.5%), the value of $f_m(D)\cdot F_f(D)$ attains only to about 10% of the initial value by the irradiation of $D_{1/5}$. Therefore, direct damage of the monomer or the filter effect does not play a main role for the observed fluorescence degradation. The quenching is most

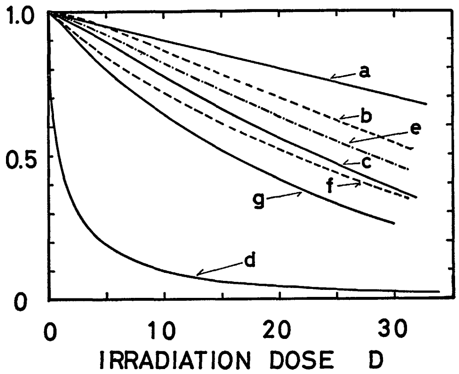

Fig. 17. Calculated curves of $F_f(D)$, $F_r(D)$, $f_m(D)$, $f_m(D)\cdot F_f(D)$, $f_m(D)\cdot F_r(D)$ and observed degradation curve for film sample of pure polyvinyltolfiene (P–95–680). (a); $f_m(D)$, (b); $F_f(D)$, (c); $f_m(D)\cdot F_f(D)$, (d); observed degradation curve for monomer-containing sample (1.45%, 1.54 mg/cm^2), (e); $F_r(D)$ for excimer fluorescence, (f); $F_r(D)$ for monomer fluorescence, (g); $f_m(D)\cdot F_r(D)$ for monomer fluorescence.

acceptable for our degradation. It is concluded that although the details of the mechanism of the fluorescence degradation are not known completely, irradiation of uv light produces some photochemical products and these products act as absorption centers in the uv wavelength region and quenching centers.

Protective effect. Just as the absorption centers which are produced in the excitation region decrease the effective excitation light, they must decrease the effective irradiation intensity when the irradiation light is the same as the excitation. Then, they act as a protective filter to further damage. This protective effect is estimated easily by integrating of eq. (18) and taking a ratio of $I_{\text{eff}}(D)$ and $I_{\text{eff}}(0)$. Then the apparent irradiation dose D must be replaced by D_{eff},

$$D_{\text{eff}}=\frac{I_{\text{eff}}(D)}{I_{\text{eff}}(0)}\cdot D=F_f(D)\cdot D \qquad (25)$$

For small irradiations, however, the filter effect and the protective effect cancel out practically.

Effect of additive anthracene. It is known that radiation damage of polymers is fairly reduced by adding a amall amount of solutes in such systems as polymethylmethacrylate-pyrene (or *p*-terphenyl).[27,28] In these cases irradiation energy does not localize in the polymers but it is transferred from polymers to additive solutes. Then the transferred energy is dissipated as the fluorescence which is characteristic of the additive solute. In our polyvinyltoluene-anthracene system, however, a definite protective effect of anthracene could not be found against the fluorescence degradation. The reason for no protection in our system is thought to be as follows. In order to have a protective effect, additive solute must have the following two properties. First, it must have a high efficiency of receiving the excitation energy from the host material. Secondly, it must be more stable than the host materials against radiation damage. In most of our samples, a fairly large amount of the monomer, which is comparable to or more than the additive anthracene, is contained and the energy transfer efficiency from the polymer to the monomer is larger than that from the polymer to anthracene. In addition to this fact, polyvinyltoluene is more stable against radiation damage than materials such as polymethylmethacrylate. Therefore, the relative stability of the additive solute to the host material is larger in polymethylmethacrylate-pyrene (or *p*-terphenyl) system than in our system.

Effect of polymerization condition. Hitherto, we did not pay any attention to the polymerization conditions such as polymerization temperature and polymerization time. With different polymerization conditions, various samples must be produced with different mean molecular weights and different concentrations of the monomer. In addition to this, irradiation of uv light may break the polymer chain.[23,27,28] The molecular weight of the polymer, that is, the chain length of the polymer was not considered in this study. As is seen from the experimental facts, however, this chain length does not seem to have any appreciable effect upon the observed fluorescence degradation. This is supported by the fact that the chain length of the polymer is currently considered to have no appreciable effect in scintillation efficiency,[16] though it was believed to be important in the early works[29,30] of plastic scintillators. Finally, it is concluded that the fluorescence degradation is affected by the polymerization conditions through the different concentrations of the residual monomer.

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References

1) N. Shiomi: J. Phys. Soc. Japan **23** (1967) 1177.
2) C. Artandi and A. A. Stonehill: Nucleonics **16** (1958) 118.
3) N. N. Winogradoffff: Nature **165** (1950) 123.
4) Z. Dezsi, J. Patko and Zs. Szentirmay: Nature **212** (1966) 751.
5) D. A. Radovsky and H. Brumberger: Nature **216** (1967) 469.
6) F. A. Black: Phil. Mag. **44** (1953) 263.
7) H. B. Clarke, D. C. Northrop and O. Simpson: Proc. Phys. Soc. **79** (1962) 366.
8) J. H. Schulman, H. W. Etzel and J. G. Allard: J. appl. Phys. **28** (1957) 792.
9) E. R. Hardwick and W. G. McMillan: J. chem. Phys. **26** (1957) 1463.
10) C. F. Sharn: J. chem. Phys. **34** (1961) 240.
11) H. Hinricks: Z. Naturforsch. **9a** (1954) 625.
12) I. M. Rozman and K. G. Zimmer: Internat. J. appl. Radiation and Isotopes **3** (1958) 36.
13) L.Ya. Zhiltsova, E. N. Matveyeva, I. M. Stoletova and M. D. Shafranov: Optics and Spectrosc. **28** (1970) 510.
14) K. Ikezaki: Japan. J. appl. Phys. **9** (1970) 936.
15) C. A. Parker: *Photoluminescence of Solutions* (Elsever, 1968). p. 220.
16) L. J. Basile: J. chem. Phys. **36** (1962) 2204.
17) L. J. Basile: Trans. Faraday Soc. **60** (1964) 1702.
18) S. S. Yanari and F. A. Bovey: Nature **200** (1963) 242.
19) J. W. Longworth: Biopolymers **4** (1966) 1131.
20) F. Hirayama, L. J. Basile and C. Kikuchi: *Organic Scintillators* ed. D. L. Horrocks (Gordon and Breach, 1968).
21) M. Leibowitz and A. Weinreb: J. chem. Phys. **46** (1967) 4652.
22) M. Ofran and A. Weinreb: J. Polymer Sci. Part A-2, **8** (1970) 161.
23) H. Aoki, A. Yoshida and T. Suzuki: J. Soc. Materials Sci. Japan **21** (1972) 309.
24) I. B. Berlman: *Handbook of Fluorescence Spectra of Aromatic Molecules* (Academic Press, 1965).
25) J. B. Birks: *Photophysics of Aromatic Molecules.* (J. Wiley, 1970) p. 572.
26) R. C. Powell: J. chem. Phys. **55** (1971) 1871.
27) D. G. Gardner and L. M. Epstein: J. chem. Phys. **34** (1961) 1653.
28) D. G. Gardner, G. Henry and D. Ward: *Energy Transfer in Radiation Processes.* ed. G. O. Phillips (Elsever, 1966).
29) S. Shimizu, F. Hirayama and S. Okamoto: Annual Rep. Res. Artif. Committee on Radioactive Isotopes **3** (1956) 48.
30) B. L. Funt and A. Hetherington: Internat. J. appl. Radiation and Isotopes **4** (1959) 189.