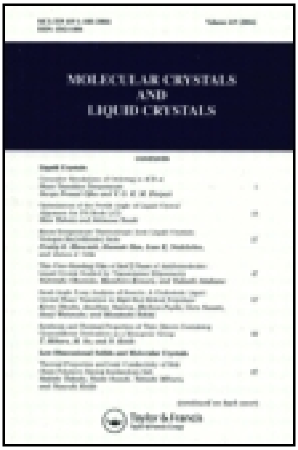

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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To cite this article: F. Hirayama , L. J. Basile & C. Klkuchi (1968): Energy Transfer and Quenching in Plastic Scintillators, Molecular Crystals, 4:1-4, 83-108

To link to this article: http://dx.doi.org/10.1080/15421406808082903

Molecular Crystals, 1968. Vol. 4, pp. 83–108

Energy Transfer and Quenching in Plastic Scintillators*†

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Abstract—Luminescence quenching in polystyrene + 9,10-diphenylanthracene + quencher and polystyrene + quencher systems has been investigated. In the latter system, the residual styrene monomer is regarded as a fluorescent solute. Result show that solvent quenching observed under uv excitation is due mainly to the competition between dipole-dipole energy transfer from polystyrene to the fluor and that from polystyrene to the quencher, and that such a transfer occurs directly from an excited polystyrene segment before it forms an excimer with an unexcited segment. Solvent quenching under beta-ray excitation was generally greater than that under uv excitation. It is suggested that this phenomenon may result from the occurrence of energy transfer at higher excited state of polystyrene. Solute quenching in some series of polystyrene + 9,10-diphenylanthracene + quencher is not accounted for by usual mechanisms of quenching. Such quenching can be explained by assuming energy transfer from the singlet excited state of 9,10-diphenylanthracene to the triplet state of the quencher.

1. Introduction

While luminescence quenching in liquid scintillators by the addition of foreign substances have been investigated extensively by many workers, very little work has been reported on the quenching in plastic scintillators.[1-4] Most studies on liquid and plastic scintillators have indicated that luminescence quenching is almost wholly attributable to the interaction between the excited solvent and the quencher, which competes with the energy transfer process from the solvent to the fluor (fluorescent

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* Work performed under the auspices of the U.S. Atomic Energy Commission.

† Based on Part II of the dissertation submitted by F. Hirayama in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan, 1963.

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solute). Quenching studies in these organic systems not only yield information on the mechanism of quenching interaction itself, but can also provide some insight into the solvent-to-fluor energy transfer process.

One of the advantages of studying energy transfer and quenching in plastic scintillators is that the rigidity of the medium hinders molecular diffusion and collision. Neglect of diffusion-controlled process in a plastic medium simplifies the correlation of observed phenomena to intrinsic properties of component compounds.

The plastic systems studied are polystyrene + fluor + quencher, and polystyrene + quencher. 9,10-Diphenylanthracene is the fluor. Six different chloro- or bromo-substituted organic compounds are used as quenchers. In the polystyrene + quencher system, the residual styrene monomer left in the sample is regarded as a fluorescent solute. It has been found that the fluorescence of thermally polymerized polystyrene is almost entirely that emitted from the residual monomer.[5, 6] The luminescence properties measured on these systems are absorption and fluorescence spectra, light output under uv and beta-ray excitation, and the decay time of fluorescence under pulsed electron excitation.

The data obtained are analyzed by typical quenching kinetics. From such analyses, the solvent quenching constant and the solute quenching constant are determined for each series studied. These quenching constants are also calculated theoretically from the optical data of the individual components of the samples, using Förster's theory of electric dipole-dipole energy transfer. Experimental and theoretical values of quenching constants are compared.

2. Experimental Procedures

Samples

9,10-Diphenylanthracene (DPA) was obtained from Pilot Chemicals, Inc., and was used without further purification. The compounds used as quenchers are listed in Table 1. These compounds were obtained from Eastman Organic Chemicals, Inc. DClB, DBrB, ClN and BrN were purified by zone melting. HClB and HClH were purified by repeated recrystallization from benzene and ethanol, respectively.

TABLE 1 Compounds Used as Quenchers

Compound	Abbreviation
p-Dichlorobenzene	DClB
p-Dibromobenzene	DBrB
Hexachlorobenzene	HClB
1,2,3,4,5,6,-Hexachlorocyclohexane	HClH
2-Chloronaphthalene	ClN
2-Bromonaphthalene	BrN

The plastic samples were prepared by thermal polymerization of solutions of DPA and/or quencher in styrene monomer without the use of an initiator. The technique of preparation has been described elsewhere.[1, 7] Polymerization was carried out at 145°C for 10 days. Standard size cylinders, 13/16 in. in diameter and 1/2 in. long, were machined from each polymerized specimen.

Three groups of sample series, given in Table 2, were prepared. For Group II the quenchers used were HClB and HClH only. For the sake of brevity, the following notations will be used hereafter to designate specific sample series or samples. To designate the sample series containing a specific quencher, the group number is followed by the abbreviated name of the quencher in parentheses, e.g., I(HClB), III(ClN). To designate the group of samples containing a specific concentration of quenchers, the value of the concentration in mole/l follows the group number, e.g., I(0.1), III(0). To designate the sample containing a specific quencher at a specific concentration, the group number is followed by both the quencher name and the concentration, e.g. II(HClH, 0.1).

TABLE 2 Sample Groups

Group	DPA concentration (mole/l. monomer)	Quencher concentration (mole/l. monomer)
Group I	0.1	0 — 0.3
Group II	0.01	0 — 0.2
Group III	None	0 — 0.3

Measurements

Absorption and fluorescence spectra

A Beckman DK-2 spectrophotometer was used for determination of uv absorption spectra. Absorption spectra of compounds and of plastic samples were measured in cyclohexane solutions. Fluorescence spectra of plastic samples were recorded on the Beckman DK-2 under front surface excitation by mercury radiation monochromatized by means of a Hilger quartz-prism monochromator. The recorded spectra were corrected for the spectral response of the spectrophotometer so that the corrected spectra gave the relative number of photons emitted as a function of wavenumber.[8]

Fluorescence intensity under uv excitation

Fluorescence intensities were measured by a Beckman DU spectrophotometer using a mercury lamp as an excitation source. Each sample was excited at two different wavelengths. One is to excite mostly polystyrene in the sample (solvent excitation). The other is to excite only DPA in Groups I and II, and in Group III to excite mostly the residual styrene monomer (solute excitation). The mercury lines chosen were: 2653 Å and 3650 Å for Groups I and II; 2653 Å and 2894 Å for Group III. The relative quantum intensity was determined by using a 0.02M solution of 1-dimethylaminonaphthalene 5-sulphonic acid in 1N NaOH as a reference solution.[9, 10]

For Group III measurements, it was necessary to correct the fluorescence intensity for reabsorption of the styrene-monomer fluorescence by the quencher in the sample. To obtain this correction a disk (0.02 in. thick) cut from a polystyrene sample containing no solute (i.e., III(0)), was placed before the sample, and was illuminated by 2653 Å radiation. The correction factor for each sample was determined from the relative intensity of the fluorescence of this disk after passing through the sample.

Scintillation intensity under beta-ray excitation

The sample was excited by beta particles from a Sr^{90} source. The scintillation was measured by an RCA 6903 photomultiplier and an associated electrometer. The scintillation intensity was expressed relative to the value obtained for an anthracene crystal having the same dimension as plastic samples.

Decay time of fluorescence

The sample was bombarded with a 75 kev pulsed electron beam, and the time variation of the fluorescence pulse was automatically recorded on a graph paper as a logarithmic intensity *vs* time curve.[11, 12] The decay time was determined from the slope of the straight line which best fits the decaying part of the semilogarithmic plot.

Immediately before any measurement of the intensity or the decay time was made, the excitation side of the sample was freshly shaved about 0.005 in. deep in order to avoid the effect of surface deterioration caused by standing in air.[13]

3. Experimental Results

Absorption Spectra

Absorption spectra of plastic samples were measured in cyclohexane solution for the samples containing 0.2 mole/l of quenchers. Careful analysis of the spectra of II(0.2) and III(0.2) indicates that these spectra are exact superposition of the spectra of individual components of the samples, including that of the residual styrene monomer. The amount of the residual monomer was determined from the specific extinction coefficient at 291 mμ after subtracting the components due to other constituents of the sample. The monomer content was found to be approximately 0.5 Wt% in all samples, regardless of the kind of quenchers, and of the presence or absence of DPA.

From these results, one may reasonably assume that little or no chemical reaction took place between the constituents of the sample during the polymerization process, that DPA and all quenchers did not inhibit the polymerization of styrene, and that the concentration of the residual monomer was practically constant (0.5 Wt%) in all the samples of Groups I, II and III.

Fluorescence Spectra

Figure 1 shows fluorescence spectra of sample I(0), II(0), III(0) and III(0.1) under the excitation by 2653 Å radiation. Fluorescence of III(0) and III(0.1) is essentially that emitted from the residual styrene monomer.[5, 6] Sample III(ClN, 0.1) does contain an appreciable amount of fluorescence from 2-chloronaphthalene. The fluorescence of I(0) is

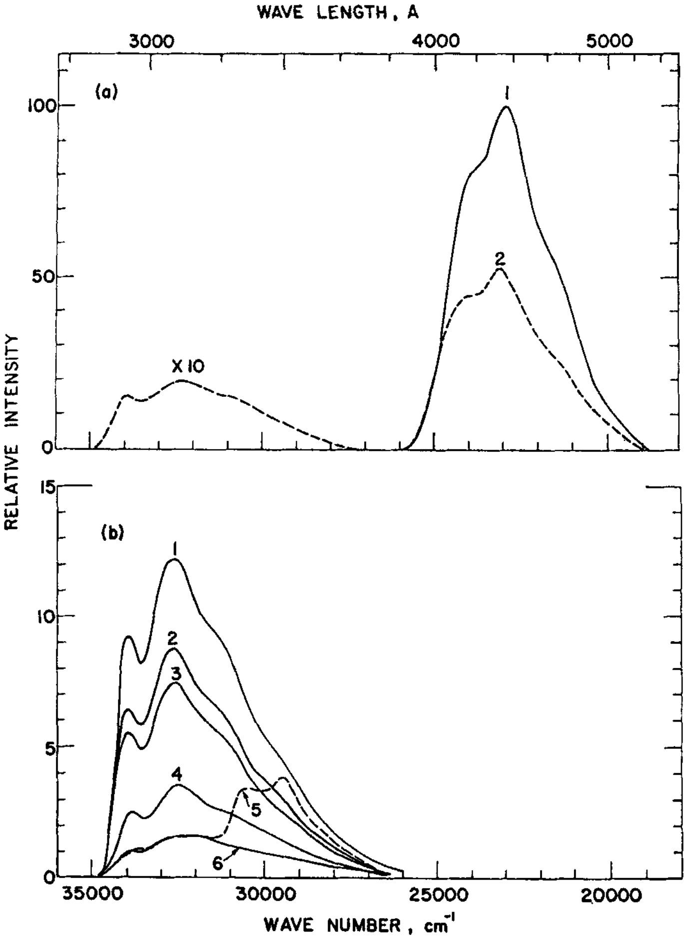

Figure 1. Fluorescence spectra of the plastic samples: (a) 1, sample I(0); 2, II(0). (b) 1, III(0) and III(HClH, 0.1;) 2, III(DClB, 0.1); 3, III(DBrB, 0.1); 4, III(HClB, 0.1); 5, III(ClN, 0.1); 6, III(BrN, 0.1). Excitation was by 2653-Å radiation. No correction was made for direct absorption of the incident radiation by the quencher.

entirely that of DPA, whereas sample II(0) contains a small amount of fluorescence from the residual monomer.

Fluorescence Intensity under UV Excitation

Results on fluorescence intensities of Groups I, II and III by uv excitation are given in Fig. 2. Figures 2a, 2b, and 2c give the data under

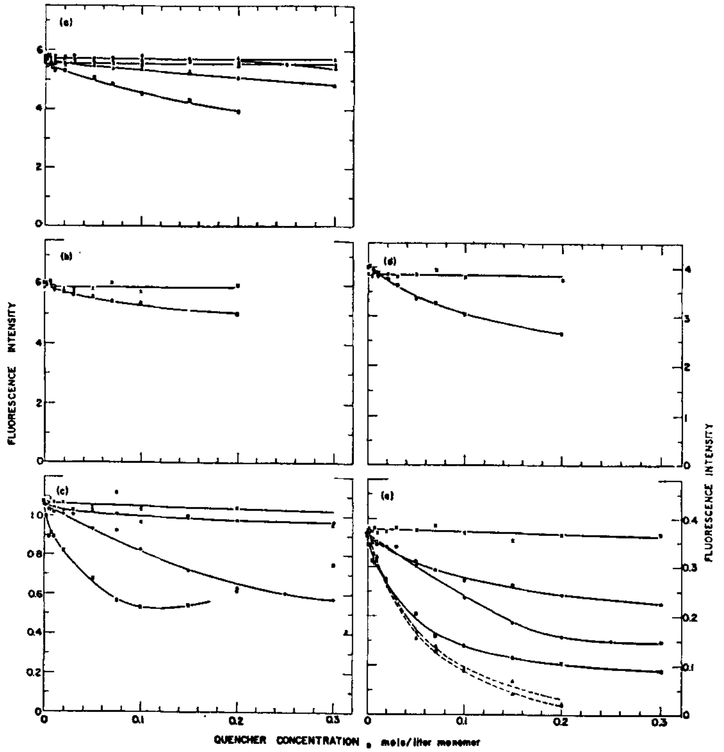

Figure 2. Fluorescence intensity under uv excitation *vs* quencher concentration: (a) Group I (3650 Å); (b) Group II (3650 Å); (c) Group III (2893 Å); (d) Group II (2653 Å); (e) Group III (2653 Å). Wavelengths of exciting radiation are given in parentheses. Quencher: ○ DClB, ● DBrB; □ HClB; × HClH; △ ClN; ▲ BrN. Solvent excitation of Group I was not possible because of high absorbance of DPA at 2653 Å. In Fig. 2c, no results are given for III(ClN) and III(BrN) under solute excitation, since both Corrections (1) and (2) were too large to be reliable. Plots for III(ClN) and III(BrN) in Fig. 2e (dotted lines) are those obtained from the peak heights at 310 mμ of their fluorescence spectra. These intensities had only Correction (1) applied, and were normalized at zero quencher concentration.

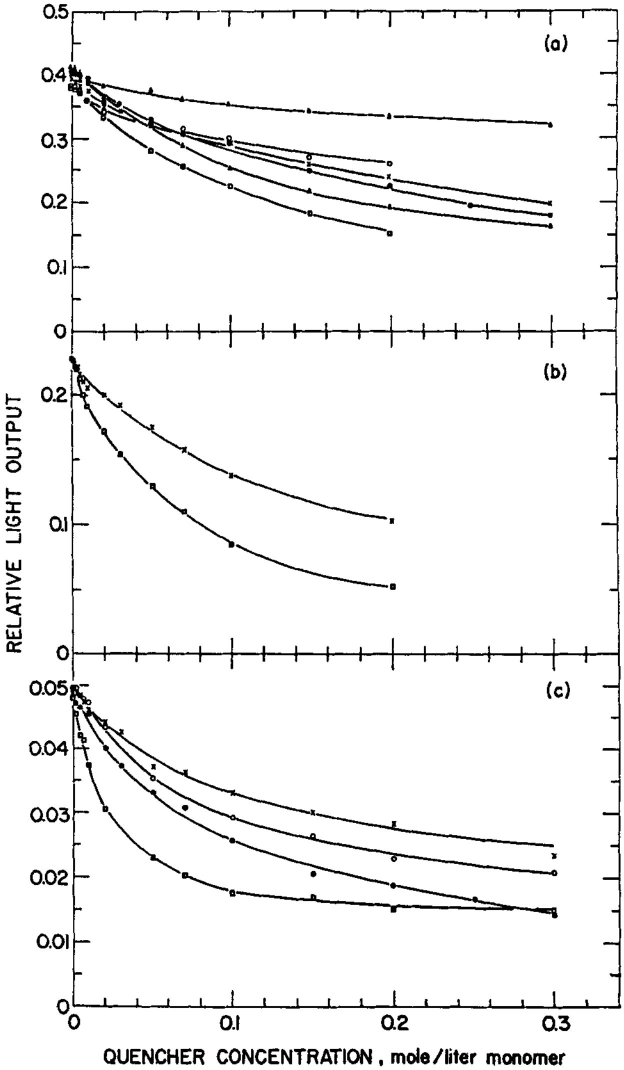

Figure 3. Scintillation intensity under beta-ray excitation *vs* quencher concentration: (a) Group I; (b) Group II; (c) Group III. Quencher: ○ DClB; ● DBrB; □ HClB; × HClH; △ ClN; ▲ BrN.

solute excitation, and Figs. 2d and 2e those under solvent excitation. Fluorescence intensities given in Fig. 2 have been corrected, where necessary, for (1) direct absorption of incident quanta by the quencher, and (2) reabsorption of fluorescence by the quencher on passing through the sample. The latter correction was applied only to Group III. (See Sec. 2.)

It is seen that HClH shows no quenching action in the three groups under both solute and solvent excitation. In Groups I and II under solute excitation, fluorescence of directly excited DPA is quenched by HClB, and to a lesser extent by BrN, whereas the remainders of the quencher do not exhibit such a quenching action.

Scintillation Intensity under Beta-Ray Excitation

Scintillation intensities of Groups I, II and III under beta-ray excitation are plotted in Fig. 3. Correction (2) described above has been applied to the intensities of Group III. All the quenchers show some quenching action in the three groups. The data shown in Fig. 3 should be compared with those in Fig. 2d and 2e for solvent excitation by uv, since the energy of beta ray is absorbed mostly by polystyrene. The striking feature of this comparison is that the scintillation intensities of Groups I, II and III containing HClH decrease appreciably on increasing quencher concentrations. As much as a 50% decrease is observed at the maximum quencher concentration, whereas no decrease is observed under solvent excitation by uv radiation.

Decay Time of Fluorescence

The decay contours of Groups I, II and III samples are found to be practically exponential. Exceptions are Group III samples containing HClB, ClN and BrN at high concentrations. Figure 4 shows the plots of the decay time *vs* quencher concentrations. Comparing with Fig. 2, one observes that the dependence of the decay time on quencher concentrations for Groups I and II follows the same trend as that obtained for the fluorescence intensity under solute excitation.

4. Quenching Kinetics

For the analysis of experimental data given in the preceding section, we employ typical quenching kinetics for a ternary system consisting

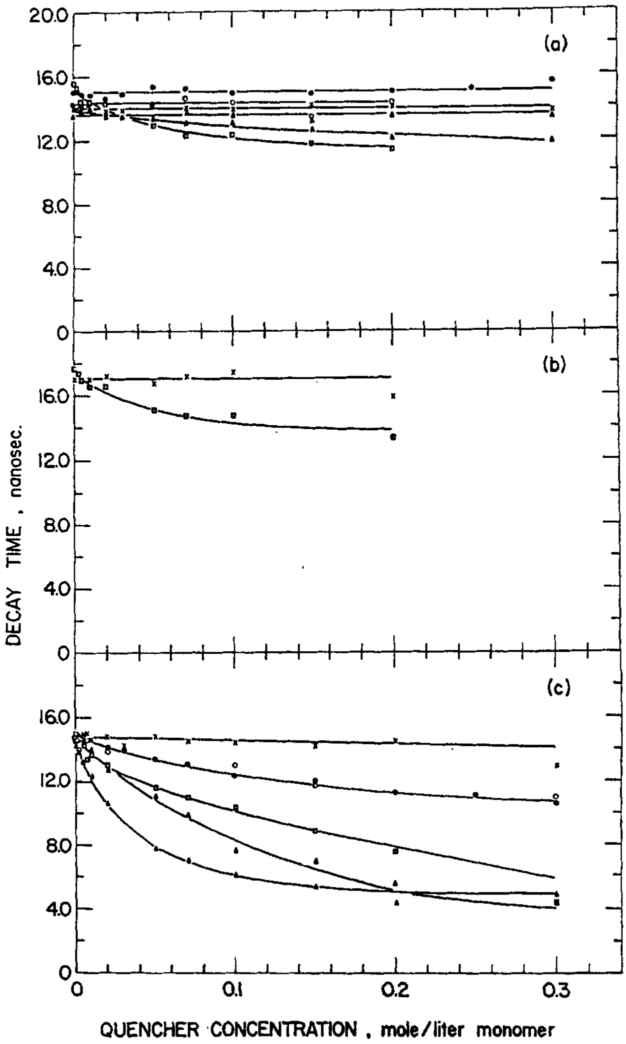

Figure 4. Fluorescence decay time *vs* quencher concentration: (a) Group I; (b) Group II; (c) Group III. Quencher: ○ DClB; ● DBrB; □ HClB; × HClH; △ ClN; ▲ BrN.

of solvent X, fluor Y and quencher Q. Hereafter, a single asterisk denotes the molecule in its lowest singlet excited state, and double asterisks that in higher singlet excited state. The kinetics is based on the following assumptions:

1. Under beta-ray excitation, only singlet states X^{**} produced in the solvent contribute to the final fluorescence from Y^*. Direct production of X^* is assumed negligible for the aromatic solvent considered here.[14] Highly excited triplet states of the solvent produced by ion recombination are ultimately dissipated into heat.

2. Internal conversion from X^{**} to X^* or to the ground state X is much faster process than any possible competing processes so that only X^* is capable of transferring energy or subject to external quenching.

3. The presence of Y and Q, whose concentrations are assumed small, does not interfere with the production of X^{**} by direct excitation by incident particles or by ion recombination.

4. All the energy transfer processes occurring in the ternary system are predominantly nonradiative, i.e., the radiative transfer process is negligible.

5. The quencher is unable either to fluoresce or to transfer energy to Y.

Intensity Relations

Let us consider a series of ternary systems in which the concentration of the fluor is fixed and that of the quencher is varied from zero to a certain value. Under the assumptions given above, we obtain the following relationships for the scintillation intensity B under beta-ray excitation, the fluorescence intensity F^X under uv solvent excitation, and the fluorescence intensity F^Y under uv solute excitation:

$$\frac{F_0^Y}{F^Y} = 1 + \beta[Q], \tag{1}$$

$$\frac{B_0}{B} \Bigg/ \frac{F_0^Y}{F^Y} = \frac{F_0^X}{F^X} \Bigg/ \frac{F_0^Y}{F^Y} = \frac{\xi_0}{\xi} = 1 + \alpha[Q], \tag{2}$$

where

$$\xi = k_Y[Y]/(k_e + k_i + k_s + k_Y[Y] + k_Q[Q]), \tag{3}$$

$$\alpha = k_Q/(k_e + k_i + k_s + k_Y[Y]), \tag{4}$$

$$\beta = k'_Q/(k'_e + k'_i + k'_s[Y]). \tag{5}$$

Here, the subscript 0 designates the value in the absence of the quencher. The quantities k_e, k_i, k_s, k_Y and k_Q are rate constants for emission, internal quenching, self-quenching, energy transfer to the fluor, and quenching by the quencher for excited solvent X^*. Similarily, k'_e, k'_i, k'_s and k'_Q are rate constants for excited fluor Y^*. Square brackets indicate the concentration in mole/l. ξ is the quantum efficiency of energy transfer from X^* to Y in the presence of Q. The quantities α and β are called the solvent quenching constant and the solute quenching constant, respectively. The relation, Eq. (2), for F^X is valid only when the exciting uv radiation for solvent excitation is not absorbed by the fluor. When direct absorption by the fluor is not negligible, the transfer efficiency ξ must be evaluated from the formula[10]

$$\xi = \frac{1}{\varepsilon_X[X]}\left\{(\varepsilon_X[X] + \varepsilon_Y[Y])\frac{F^X}{F^Y} - \varepsilon_Y[Y]\right\}, \tag{6}$$

where ε_X and ε_Y are the molar extinction coefficients of X and Y, respectively, at the wavelength of solvent excitation. One should note that Eq. (2) predicts the solvent quenching constant α to be the same whether determined from the scintillation intensity B or from the fluorescence intensity F^X, and that this is a consequence of Assumptions 2 and 3.

Intensity vs Time Relations

Suppose that the solvent of the ternary system is instantaneously excited at $t = 0$ by a pulse of uv or electrons. The intensity *vs* time relation for the fluorescence pulse emitted from the fluor is expressed by[15-17]

$$F^X(t) = aB(t) = A_\tau\left(\frac{e^{-\frac{t}{\tau_X}} - e^{-\frac{t}{\tau_Y}}}{\tau_X - \tau_Y}\right), \tag{7}$$

where

$$\tau_X = 1/(k_e + k_i + k_s + k_Y[Y] + k_Q[Q]), \tag{8}$$

$$\tau_Y = 1/(k'_e + k'_i + k'_s[Y] + k'_Q[Q]). \tag{9}$$

A_τ and a are constants which are independent of time. τ_X is the reciprocal of the sum of all rate constants for X^*, and is therefore the mean lifetime of X^* in the ternary system. Similarly, τ_Y is the mean lifetime of Y^*. From Eqs. (4), (5), (8), and (9), one gets the relations

$$\tau_{X0}/\tau_X = 1 + \alpha[Q], \tag{10}$$

$$\tau_{Y0}/\tau_Y = 1 + \beta[Q], \tag{11}$$

where τ_{X0} and τ_{Y0} are lifetimes in the absence of the quencher. The decay time τ determined from the decaying part of the fluorescence pulse corresponds to either τ_X or τ_Y depending on whether $\tau_X > \tau_Y$ or $\tau_X < \tau_Y$, respectively. If it is possible to decide to which of τ_X and τ_Y the measured decay time τ corresponds, either α or β can be determined from Eq. (10) or (11).

5. Analysis of Experimental Data

Determination of experimental values of quenching constants α and β is made from the slope of the straight line fitted by a least-squares method to the plots of ξ_0/ξ, F_0^Y/F^Y and τ_0/τ [Eqs. (1), (2), (10) and (11) in Sec. 4]. Hereafter, the superscripts B, F and τ will be appended to α and β to designate that the quenching constants are determined from the data of the scintillation intensity, the fluorescence intensity and the decay time, respectively. In determining α^F from Eq. (2), values of ξ evaluated by Eq. (6) were used, since direct excitation of the fluor under solvent excitation was not negligible for all the sample series.

Slopes of the plots τ_0/τ for Groups I and II are assigned as the solute quenching constant β^τ. This is based on the results of Basile and Weinreb on DPA-polystyrene scintillators.[13] Their results indicate that the measured decay time τ, at high solute concentration, corresponds to the lifetime of excited DPA, i.e., τ_Y in Eq. (7). In contrast, slopes of the plots τ_0/τ for Group III are assigned as the solvent quenching constant α^τ. The reason is as follows. The decay time of the fluorescence of a very dilute solution of styrene monomer in nitrogenated cyclohexane is 9.4 nsec.[6] This value may be considered as an approximate upper limit of the lifetime of excited residual monomer in the polystyrene medium. Then the decay time of sample III(0), which is 14.5 nsec, should correspond to the lifetime of excited polystyrene with the presence of the residual monomer, i.e., τ_X in Eq. (7).

All the experimental values of α and β obtained by the above procedures are divided by a factor 1.16 to take into account the actual increase in quencher concentrations due to the shrinkage of polystyrene upon polymerization.[18] The least-squares estimates of experimental values of α and β with their standard deviations will be given in Tables 4 and 5 in Sec. 7, where these values are compared with theoretical values which will be calculated in the next section.

6. Theoretical Values of Quenching Constants

The theoretical calculation of the solvent quenching constant α and the solute quenching constant β for each sample series of Groups I, II and III is based on the following assumptions: (1) solvent quenching is due to energy transfer from polystyrene to the quencher, which competes with energy transfer from polystyrene to the fluor; (2) solute quenching is due to energy transfer from the fluor to the quencher; and (3) electric dipole-dipole transfer mechanism is responsible for all the energy transfer processes occurring in our plastic ternary systems.

Formulas for Quenching Constants α and β

The expression for the transfer efficiency $\xi_{D\rightarrow A}$ for dipole-dipole energy transfer from energy donor D to energy acceptor A distributed randomly in solution has been given by Förster.[19, 20] This expression can be approximated, without an appreciable error, by a function of Stern-Volmer type:[20]

$$\xi_{D\rightarrow A} = \frac{2.05[A]}{[A_0]} \Bigg/ \left(1 + \frac{2.05[A]}{[A_0]}\right), \tag{12}$$

where $[A]$ is the acceptor concentration in mole/l, $[A_0]$ is the critical transfer concentration which is related to the critical transfer distance R_0 by

$$[A_0] = 3000/4\pi N R_0^3. \tag{13}$$

R_0 can be calculated from the optical data of the donor and acceptor by the well-known Förster's formula.[21] The value of the orientation factor $\varkappa$ appearing in the Förster's formula is $\sqrt{2/3}$ for fast-rotating molecules, and is $0.845\sqrt{2/3}$ for molecules with fixed orientations.[22] Thus, the value of $[A_0]$ for the fixed-orientation case is 1/0.845 times that for the fast-rotating case.

From Eqs. (3), (4), (5) and (12), we obtain the following expressions for theoretical values of α and β:[23]

$$\alpha_{\text{calc}} = \frac{2.05}{[Q_0]_X} \Bigg/ \left(1 + \frac{2.05[Y]}{[Y_0]_X}\right), \tag{14}$$

$$\beta_{\text{calc}} = \frac{2.05}{[Q_0]_Y}, \tag{15}$$

where $[Y_0]_X$, $[Q_0]_X$ and $[Q_0]_Y$ correspond to $[A_0]$ in Eq. (12), and are critical transfer concentrations for solvent-to-fluor transfer, solvent-to-quencher transfer and fluor-to-quencher transfer, respectively.

Calculation of Quenching Constants

To obtain theoretical values of the solvent quenching constant α from Eq. (14) one must first calculate the critical transfer concentration $[Y_0]_X$ and $[Q_0]_X$ for donor-acceptor pairs – polystyrene-fluor and polystyrene-quencher. It is at this point that excimer formation in polystyrene molecules must carefully be taken into account. As described in the Appendix, an excited phenyl segment of polystyrene efficiently forms an excimer with an unexcited segment both in liquid solution and in solid phase. Energy transfer from polystyrene to the solute may take place through two paths: direct transfer from the excited segment before excimer formation occurs, and transfer from the excimer after it has been formed. Since the treatment of our ternary systems considering these two paths of transfer processes is quite involved, the following cases are chosen as two extremes:

Case S: Direct energy transfer from the excited segment to fluor or to quencher is much more efficient than the process of excimer formation.

Case D: Excited segment forms an excimer much more efficiently than its spontaneous deactivation and transfer processes so that energy transfer to fluor or to quencher takes place only from the excimer.

The critical transfer concentrations $[Y_0]_X$ and $[Q_0]_X$, and subsequently the quenching constant α, are calculated for both Case *S* and Case *D*. In evaluating the critical transfer distance R_0 from Förster's formula, the fluorescence spectrum $f_D(\nu)$ and the fluorescence yield η_D of ethylbenzene, a segment-analog of polystyrene, were used for Case *S*. For Case *D*, $f_D(\nu)$ and η_D used were those of the polystyrene excimer. (See Appendix.)

Table 3 summarizes the values of the spectral overlap J of donor-emission and acceptor-absorption spectra, the critical transfer distance R_0 and the critical transfer concentration $[A_0]$ for all donor-acceptor pairs in our plastic samples. The values of α and β are determined by putting $[A_0]$ given in Table 3 into Eqs. (14) and (15), respectively.

TABLE 3 Values of Spectral Overlap J, Critical Transfer Distance R_0 and Critical Transfer Concentration $[A_0]$ for Donor-Acceptor Pairs in the Plastic Samples

Donor	Acceptor	$J \times 10^{18}$		R_0(Å)†		$[A_0]$ (mole/l)†	
		$J^{(S)}$	$J^{(D)}$	$R_0^{(S)}$	$R_0^{(D)}$	$[A_0]^{(S)}$	$[A_0]^{(D)}$
Polystyrene	DPA	2370	4530	17.5	13.7	0.0740	0.152
	Styrene monomer	266	6.2	12.2	4.5	0.220	4.10
	p-Dichlorobenzene	89	1.3	10.2	3.5	0.382	8.94
	p-Dibromobenzene	89	1.2	10.2	3.5	0.381	9.38
	Hexachlorobenzene	136	21	10.9	5.6	0.308	2.22
	Hexachlorocyclohexane	0	0	0	0	∞	∞
	2-Chloronaphthalene	1830	162	16.8	7.9	0.0842	0.802
	2-Bromonaphthalene	1950	168	17.0	8.0	0.0814	0.786
DPA	All quenchers	0		0		∞	
Styrene monomer	p-Dichlorobenzene	0.44		3.8		6.61	
	p-Dibromobenzene	0.75		3.6		5.05	
	Hexachlorobenzene	79		9.1		0.533	
	Hexachlorocyclohexane	0		0		∞	
	2-Chloronaphthalene	326		11.7		0.242	
	2-Bromonaphthalene	373		11.8		0.226	

† Values calculated for the fast-rotating case. R_0 and $[A_0]$ for the fixed-orientation case are $\sqrt[3]{0.845}$ and 1/0.845 times, respectively, of these values.

7. Comparison of Experimental and Theoretical Values of Quenching Constants

Tables 4 and 5 compare the experimental and theoretical values of the solvent quenching constant α and the solute quenching constant β, respectively. Since our samples are plastic solid solutions, it appears appropriate to use theoretical values calculated for the fixed-orientation case. Those calculated for the fast-rotating case are also given for comparison purposes.

Comparison of α^F and α^τ with α_{calc}

Values of $\alpha^{(S)}$ are generally in fair agreement with available values of α^F or α^τ. Values of $\alpha^{(D)}$ are much smaller than these experimental values. (See Table 4.)

These results support the interpretation that the major cause of solvent quenching occurring at the lowest excited state of polystyrene results from the competition in the energy transfer process between polystyrene to fluor and polystyrene to quencher. This transfer process occurs by dipole-dipole interaction directly from the excited segment before excimer formation takes place, i.e., our Case *S* mechanism. This suggests that contributions to solvent quenching by other mechanisms, for example complex formation, external heavy-atom effect, etc., are relatively of minor importance.

Solvent-to-fluor transfer efficiencies, in samples II(0) and III(0), calculated for Case *S* are in much better agreement with experimental values than those calculated for Case *D*. Our analysis of data obtained by Swank and Buck for nine different polystyrene-fluor systems also favors Case *S* transfer.[23, 24]

These results have an important bearing on the problem of energy migration through the polystyrene medium. This problem is related to the interpretation of excimer formation in solid polystyrene. The fluorescence spectrum of a film of polystyrene consists of the excimer band only. (See Appendix.) This indicates that excimer formation in solid polystyrene occurs with about 100% efficiency. To explain this high efficiency one can consider the following two extremes (1) An originally excited segment can form an excimer with the closest segment with 100% efficiency, regardless of whether they belong to the same or different polystyrene chain; (2) The probability of an originally excited segment to

TABLE 4 Comparison of Experimental and Theoretical Values of the Solvent Quenching Constant α (l. polymer · mole^{-1})†

Quencher	Group I			Group II				Group III				
	α_{exp}	α_{calc}		α_{exp}		α_{calc}		α_{exp}			α_{calc}	
	α^B	$\alpha^{(S)}$	$\alpha^{(D)}$	α^B	α^F	$\alpha^{(S)}$	$\alpha^{(D)}$	α^B	α^F	α^τ	$\alpha^{(S)}$	$\alpha^{(D)}$
p-Dichloro-benzene	2.02 ±.11	1.22 (1.27)	0.08 (0.09)	—	—	3.58 (4.05)	0.17 (0.20)	4.39 ±.27	2.59 ±.12	1.22 ±.10	3.24 (3.64)	0.19 (0.22)
p-Dibromo-benzene	3.19 ±.09	1.22 (1.27)	0.08 (0.09)	—	—	3.58 (4.05)	0.16 (0.19)	3.76 ±.19	2,74 ±.20	1.21 ±.09	3.24 (3.64)	0.18 (0.21)
Hexachloro-benzene	3.32 ±.04	1.52 (1.58)	0.33 (0.36)	11.0 ±.2	2.42 ±.16	4.44 (5.02)	0.68 (0.79)	3.02 ±.37	3.94 ±.30	3.86 ±.15	4.03 (4.52)	0.77 (0.91)
Hexachloro-cyclohexane	2.75 ±.08	0 (0)	0 (0)	4.96 ±.09	0.30 ±.16	0 (0)	0 (0)	3.20 ±.22	−0.10 ±.09	0.09 ±.06	0 (0)	0 (0)
2-Chloro-naphthalene	0.72 ±.05	5.55 (5.77)	0.92 (0.99)	—	—	16.3 (18.5)	1.91 (2.22)	—	—	10.4 ±.7	14.7 (16.5)	2.12 (2.51)
2-Bromo-naphthalene	3.72 ±.16	5.74 (5.96)	0.94 (1.01)	—	—	16.9 (19.2)	1.95 (2.26)	—	—	6.69 ±.25	15.2 (17.2)	2.16 (2.56)

† Theoretical values $\alpha^{(S)}$ and $\alpha^{(D)}$ without parentheses are those calculated for molecules with fixed orientations. Values in parenthese are those calculated for fast-rotating molecules.

form an excimer is, on the average, relatively small. However, the energy of the excited segment migrates through the polystyrene medium with high efficiency until excimer formation takes place at the site where two segments happen to be arranged very favorably.

Our findings, which favor Case S transfer, is in direct contradiction to (1). If this situation were valid, energy transfer to the dissolved solute would occur predominantly from excimers, i.e., by Case D transfer. If (2) is more nearly correct, then energy transfer will take place directly from an excited segment during the energy migration from segment to segment; our Case S mechanism. It appears therefore that our results favor the occurrence of efficient energy migration in solid polystyrene. This is in agreement with the proposal made by Brown, Furst and Kallmann from different viewpoints.[2]

Comparison of α^B with α^F

Examination of the data in Table 4 shows that α^B values for Groups I, II and III are appreciably higher than values of α^F or $\alpha^{(S)}$ with a few exceptions. Values for α^F are not available for Group I. From our previous discussion we may assume that $\alpha^{(S)}$ for Group I represents an approximate value of α^F for this group.[26] According to the quenching kinetics (Sec. 4), α must be the same regardless of whether it was determined from intensity data obtained by beta-ray excitation or uv excitation. This is a direct consequence of Assumptions 2 and 3 made in Sec. 4. Our data on α^B indicate that one, or both, of these assumptions is not valid.

The data in Tables 4 and 5 show that the available values of α^F, α^τ, β^F and β^τ, for the series I, II, III (HClH), are practically zero. This indicates that neither polystyrene nor the fluor, in the lowest excited state, is quenched by hexachlorocyclohexane. The marked degree of quenching under beta-ray excitation, as noted by the relatively large values of α^B, must result from interactions involving higher excited states or ionized states.

At the quencher concentrations used it is evident that direct excitation of the quencher is not responsible for the large decrease, about 50%, observed in the scintillation intensity. (See Fig. 3.) The external heavy-atom effect, in this case enhancing singlet-to-triplet conversion at higher excited states, is probably of minor importance.

The marked degree of solvent quenching can be accounted for, if an appreciable fraction of the energy is transferred to HClH from higher excited states of the solvent. As seen from Table 4, the value of α^B for II (HClH) is about two times as great as for I(HClH). The DPA concentration is ten times greater in the latter series. Transfer at higher excited states can provide a plausible explanation for the dependence of α^B on the fluor concentration. Energy transfer from X^{**} to HClH will compete more effectively with that from X^{**} to DPA in II(HClH) than it does in I(HClH).

Another plausible explanation for the high solvent quenching is that ion-recombination process is dominant. Such a process would produce highly excited solvent molecules to an appreciable degree. The quencher molecule would interfere with this ionic process of solvent excitation by capturing free electrons. This is essentially the same mechanism proposed by Lipsky *et al.*, for a possible explanation of their results on quenching by bromobenzene in p-terphenyl-benzene systems.[27]

At present for an explanation of our results on α^B and α^F we tend to prefer energy transfer involving higher excited states of the solvent for the following reason. For an organic scintillator under electron excitation (beta- or gamma-ray excitation), the fraction of the luminescence output resulting from the ion-recombination process is expected to be at most 1/9 of the total light output.[28, 29] This estimate follows from assumptions that the relative probabilities of excitation and ionization in an organic molecule are approximately 2 : 1, and that statistically only 1/4 of the excited molecules formed by ion recombination will be left in excited singlet states.[28-31] If this estimate is reasonable, the decrease in light output cannot be more than 1/9, even if the ion-recombination process is completely prohibited by the presence of the quencher. To account for the 50% decrease in the scintillation intensities, the relative probabilities of excitation and ionization would have to be 1 : 4 (instead of 2 : 1).

Needless to say, it would be premature to exclude quenching involving the ion-recombination process, or other processes not discussed, on the basis of the above argument. At present we feel that transfer of energy involving higher excited states is the simplest explanation. Information on optical excitation in the vacuum uv may help resolve this problem.

For the remaining series of Groups I, II, and III, energy transfer can occur from the lowest excited state X^* to the quencher in direct competition with transfer from X^* to the fluor. To attribute the results of

α^B and α^F to transfer involving X^{**}, it is necessary to assume that the ratio of the rate constant for polystyrene-to-quencher transfer to that for polystyrene-to-fluor transfer at X^{**} states, averaged over all X^{**} states, is larger than such a ratio at X^* state.

The noticeable exception to comparing solvent quenching constants is in I(ClN). In this case α^B is much smaller than $\alpha^{(S)}$. This anomaly can be explained by taking into account energy transfer from 2-chloronaphthalene to DPA. This process was neglected in calculating $\alpha^{(S)}$.[23]

Comparison of β^F and β^τ with β_{calc} for Groups I and II

The theoretical values of β are zero for all series of Groups I and II (Table 5). The values of β^F and β^τ for I, II(HClB) and for I(BrN) are larger than zero and approximately of the same magnitude. Values of β_{exp} for the remaining series are practically zero in agreement with β_{calc}.

TABLE 5 Comparison of Experimental and Theoretical Values of the Solute Quenching Constant β (l. polymer·mole^{-1}).†

Quencher	Group I			Group II			Group III	
	β_{exp}		β_{calc}	β_{exp}		β_{calc}	β_{exp}	β_{calc}
	β^F	β^τ		β^F	β^τ		β^F	
p-Dichlorobenzene	0.00 ±.05	0.10 ±.10	0 (0)	—	—	0 (0)	0.34 ±.08	0.26 (0.31)
p-Dibromobenzene	0.16 ±.03	−0.02 ±.04	0 (0)	—	—	0 (0)	2.66 ±.11	0.34 (0.41)
Hexachlorobenzene	1.80 ±.06	1.79 ±.24	0 (0)	0.88 ±.08	1.37 ±.18	0 (0)	8.87 ±.57	3.25 (3.85)
Hexachlorocyclohexane	0.06 ±.02	0.03 ±.03	0 (0)	0.00 ±.08	0.25 ±.12	0 (0)	0.09 ±.10	0 (0)
2-Chloronaphthalene	0.04 ±.03	0.12 ±.04	0 (0)	—	—	0 (0)	—	7.15 (8.47)
2-Bromonaphthalene	0.51 ±.03	0.56 ±0.4	0 (0)	—	—	0 (0)	—	7.65 (9.05)

† Theoretical values of β without parentheses are those calculated for molecules with fixed orientations. Values in parentheses are those calculated for fast-rotating molecules.

To explain the rather large values for β^F and β^τ in the above mentioned systems, one must consider quenching mechanisms other than the ordinary energy transfer from the fluor to the quencher. Since β^F and β^τ are about the same, this indicates that quenching occurs after DPA molecules have been excited. Thus, quenching due to complex formation can be ruled out. The external heavy-atom effect is also inadequate to explain this quenching, since no quenching is observed by DBrB. The possibility that energy of an excited DPA may be transferred to the triplet state of the quencher is plausible. Energetically such a transfer is possible for systems involving ClN, BrN and HClB. Triplet levels of these molecules, in fact, lie below the excited singlet state of DPA.[32,33] Triplet levels of the remaining quenchers lie above it.[32]

We have calculated the quenching constants $\beta_{S\to T}$ for ClN and BrN. For this calculation we assumed that the singlet-to-triplet transfer occurs by dipole-dipole interaction.[23] Singlet-triplet absorption coefficients of the quenchers were estimated from their phosphorescence data.[23,32,34] Our results for $\beta_{S\to T}$ are 0.05 for ClN and 0.25 for BrN. The former is of the order of experimental errors in the present experiment; the latter about one half of experimental values. The discrepancy between β_{exp} and $\beta_{S\to T}$ for I(BrN) may be due to the large error involved in estimating the singlet-triplet absorption coefficient. Therefore, we conclude that the singlet-to-triplet energy transfer is, at least, in part responsible for the observed solute quenching in I(BrN). Owing to the lack of reliable phosphorescence data of HClB, $\beta_{S\to T}$ could not be calculated for I, II(HClB). It seems reasonable to assume that a similar explanation can be given for these series, since $\beta^F \simeq \beta^\tau$.

8. Summary

Investigations have been made on luminescence quenching in polystyrene + 9,10-diphenylanthracene + quencher and polystyrene + quencher systems with the use of six different chloro- or bromo-substituted organic compounds as quenchers. In the latter system, the residual styrene monomer is regarded as a fluor. The results have indicated that (1) the competition between energy transfer from polystyrene to the fluor and that to the quencher is mainly responsible for solvent quenching under uv excitation; (2) these transfer processes occur by dipole-dipole transfer mechanism directly from excited polystyrene segment before it forms an excimer; (3) efficient energy migration takes place through the polystyrene medium; (4) higher degree of solvent quenching under beta-ray excitation than under uv excitation may result from energy transfer involving highly excited states of polystyrene; and (5) singlet-to-triplet energy transfer from the fluor to the quencher may be responsible for solute quenching in some sample series.

Acknowledgements

The authors are indebted to Drs. I. B. Berlman, R. K. Swank and W. L. Buck for helpful discussions. They also wish to thank R. Marema for his technical assistance throughout the experimental phase of the investigation.

Appendix: Excimer Formation in Polystyrene

Figure 5 shows absorption and fluorescence spectra of ethylbenzene (a segment-analog of polystyrene) and polystyrene in solution, and a film of polystyrene (monomer-free). Whereas the absorption spectra of ethylbenzene and polystyrene are almost the same, the fluorescence spectra are entirely different from each other. The spectrum of polystyrene in solution consists of two bands, the 280 mμ band and the 330 mμ band, which we call an S band and a D band, respectively. The D band is attributed to the emission from an excimer (a transient dimer) formed by the association of excited and unexcited phenyl segments, and the S band to the emission from an unassociated segment. The relative intensities of the S and D bands are found to be independent of the polystyrene concentration, indicating that the excimers are formed intramolecularly.

From a kinetic analysis, efficiencies Φ of excimer formation are calculated to be 0.99, 0.98 and 0.97 in cyclohexane, p-dioxane and 1,2-dichloroethane, respectively. This dependence of Φ on the solvent is attributed to the difference in the goodness of the solvent. The fluorescence quantum yield η of the excimer in cyclohexane solution is calculated to be 0.02, and that of ethylbenzene 0.18. (These values of η were used in calculating the critical transfer distance R_0 in Sec. 6.) The fluorescence spectrum of the film of polystyrene consists of the D band only indicating that excimer formation in solid polystyrene occurs practically with 100% efficiency. Readers are referred to Refs. 6 and 35 for more detailed results and discussions on intramolecular excimers in polystyrene, related polymers and copolymers, and in diphenyl and triphenyl alkanes.

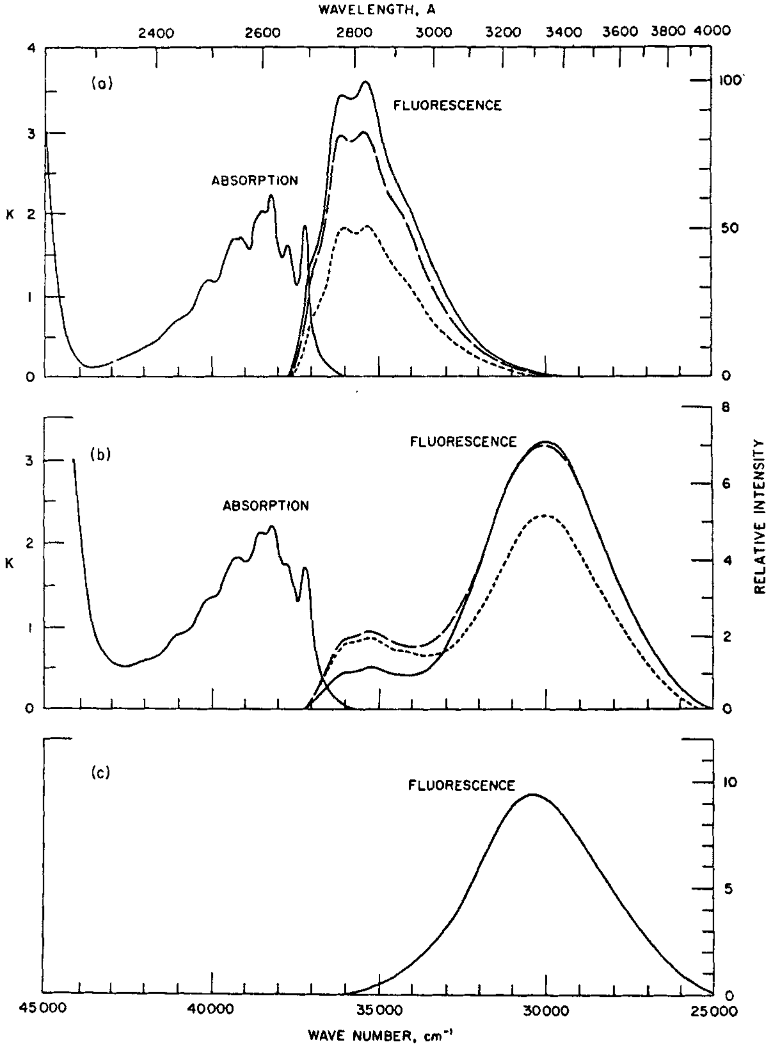

Figure 5. Absorption and fluorescence spectra of: (a) ethylbenzene in solution; (b) polystyrene in solution; (c) a film of polystyrene. Solvent: (—) cyclohexane; (— — —) p-dioxane; (- - - - - -) 1,2-dichloroethane. Fluorescence spectra in (a) and (b) are those measured on 0.01*M* nitrogenated solution. Excitation was by 2537 Å radiation.

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