Energy Transfer Processes Between Primary and Secondary Dopants in Polystyrene Solutions Dissolved in 1,4-Dioxane

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ABSTRACT: High molecular weight polystyrene prepared by emulsion polymerization was characterized by gel permeation chromatography, differential scanning calorimetry, and solution viscosity. Prepared polystyrene was used to study the energy transfer processes using Exalite 416 and Coumarin 515 dyes as the primary and the secondary dopants. Absorption and emission spectra of the dyes in polystyrene (PS) solution of concentration 2.5 g/dL in 1,4-dioxane have been measured. Absorption spectrum of the acceptor dye, Coumarin 515 (wavelength shifter), at 403 nm matches with the emission spectrum of the donor dye, Exalite 416. Continuous wave emission spectra of these wavelength shifters have been studied by changing the concentration of Coumarin 515 dye (accepter) while keeping the Exalite 416 (donor) concentration (10^{-4} M) fixed in the PS solution. Energy transfer process has been discussed. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 336–341, 2005

Key words: energy transfer; fluorescence; dyes; polystyrene; UV-VIS spectroscopy

INTRODUCTION

Polystyrene (PS) is one of the most widely studied polymers in understanding the spectroscopic[1–4] and thermodynamic interactions in solution.[5–7] Polystyrene and methyl polystyrenes have been widely used as plastic scintillators[8] in medical imaging and high-energy physics. It is, therefore, important to study the energy transfer processes and spectral shift of the dyes in PS solutions of different concentrations dissolved in a suitable solvent.[9–12] A typical plastic scintillator consists of a PS matrix in which primary (donor) and secondary (acceptor) dopants are added in small quantities. Then, by passing high-energy radiation through such a system, UV fluorescence in the base PS matrix is produced. This radiation energy is emitted by the donor and absorbed by the acceptor. Suitable organic dyes are generally used as donors and acceptors.[13,14]

To investigate these effects, polystyrene was prepared by the emulsion polymerization technique. The polymer was characterized by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and solution viscosity measurements. Two dyes, namely, Exalite 416 and Coumarin 515, have been used as the primary and secondary dopants by observing their overlap in emission and absorption spectra, respectively, in PS solution. Excitation of PS leads to UV light, which gets quickly absorbed by the primary dopant. The acceptor Coumarin, which finally emits in the red, absorbs the blue radiation from the donor Exalite. Typical commercially available plastic scintillators of this type have decay times of only a few nanoseconds. However, the present article deals with the wavelength shifters based on mixtures of Coumarin and Exalite dyes.

EXPERIMENTAL

Materials

Styrene monomer was purchased from Aldrich Chemical Company, Wisconsin, USA. Analytical grade 1,4-dioxane, sodium laurylsulfate, and potassium persulfate were purchased from S.D. Fine Chemicals, Mumbai, India. Coumarin 515 [3-(1-methylbenzimidazol-2-yl)-7-diethylaminocoumarin] ($C_{21}H_{21}N_3O_2$) having MW 347, and Exalite 416 [1,1,1′1′-tetraethyl-5,5′-diparaanisyl-[2,3:5,6] diindanobenzene] ($C_{46}H_{50}O_2$) having MW 711, were purchased from Exciton, USA.

Synthesis of polystyrene by emulsion polymerization

In a four-necked 250 mL round bottom flask containing 100 mL distilled water equipped with a mechanical stirrer, condenser, nitrogen inlet, and dropping

funnel, 2 g of sodium laurylsulfate (emulsifier) and 20 mg of potassium persulphate (initiator) were dissolved. To this mixture, 10 mL of destabilized monomer was added dropwise for about 20 min. The temperature of the reaction mixture was maintained around 60–70°C for 4 h. Turbidity appears at the end of the reaction, and the emulsion was broken down by adding a saturated NaCl solution. The PS formed was filtered by vacuum filtration and washed three to four times with distilled water to remove the emulsifier. The solid polymer was dried at 40°C in a vacuum oven for 4 h.

Differential scanning calorimetry (DSC)

Thermal analysis was performed on the PS using DSC, with model DSC SP, Rheometric Scientific, UK. Thermograms were recorded from 25 to 400°C at the heating rate of 10°C/min under nitrogen atmosphere.

Molecular weight determination

Gel permeation chromatography (GPC)

Molecular weight of the PS was determined using GPC model VE 1122, Visoctek, Houston, Texas, USA, with triple detectors. The columns used were of viscoGEL GMHHRH. Tetrahydrofuran was used as a mobile phase. About 1 mg/mL polymer solution was prepared, and 300 μL solution was loaded into the column. The GPC experiment was run for 30 min.

Viscosity measurements

Dilute solution viscosities of different PS concentrations in toluene were measured at 30°C using a Scott-Gerate Viscometer (model AVS 350, Hofheim, Germany). The viscometer performs automated measurements of flow-through times in capillary tubes. Efflux times were determined on a digital display to an accuracy of ± 0.01 s. Temperature of the bath (Scott-Gerate, model CT 050/2, Hofheim, Germany) was maintained constant at 30°C within an accuracy of 0.01°C. Approximately 5 cm^3 volume of the liquid was taken in the viscometer tube. The liquid was allowed to equilibrate to the desired bath temperature for about 10 min.

Preparation of polystyrene scintillator base matrix

The scintillator matrix was prepared by dissolving Exalite and Coumarin in the PS solution prepared in 1,4-dioxane. To study the energy transfer from donor Exalite to acceptor Coumarin as a function of concentration of accepter, at a fixed concentration of the donor, six different solution systems were prepared by adding (a) 13.3 μM, (b) 16.6 μM, (c) 20 μM, (d) 26.2
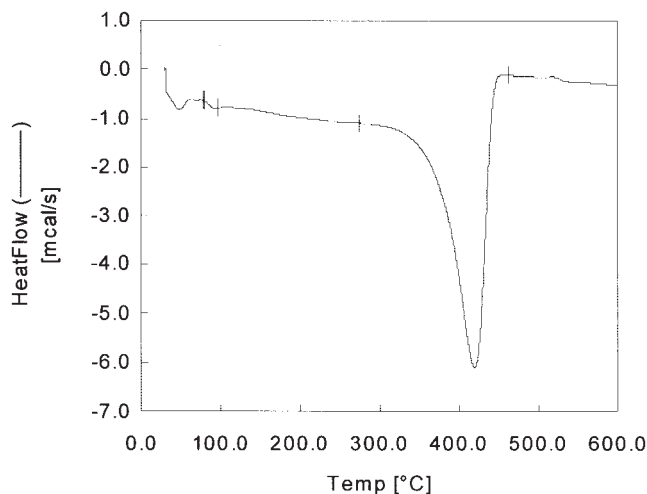

Figure 1 DSC curve of polystyrene.

μM, (e) 30 μM, and (f) 33.3 μM of Coumarin to PS solution of concentration 2.5 g/dL containing 10^{-4} M Exalite.

Absorbance and fluorescence measurements

Fluorescence measurements were carried out on a Hitachi model F-2000 fluorescence spectrophotometer (Tokyo, Japan). The light source for the fluorescence spectrophotometer was a 150 W xenon lamp with ozone self-dissociation function. The wavelength accuracy was better than ± 1 nm. The continuous wave emission spectra of polymer solutions containing the fluorescence spectra of the two dopants were recorded at the excitation wavelength of Exalite, 353 nm. The absorption spectrum was recorded with a Hitachi model 150–20, UV-VIS spectrophotometer with wavelength accuracy of ± 0.4 nm.

RESULTS AND DISCUSSION

Polymer characterization

A 92.2% yield of PS was obtained by emulsion polymerization. DSC characterized the PS for its glass transition temperature and melting point. The curve is shown in Figure 1. Peaks at 90.41°C and 412°C represent the glass transition and melting points of PS, respectively.

The molecular weight of the PS was determined by GPC and viscosity experiments. Retention volume versus response of GPC is shown in Figure 2. Different average molecular weights of PS are: $\bar{M}_n$ = 2,39,536, $\bar{M}_w$ = 3,80,292, $\bar{M}_\eta$ = 2,85,013, and $\bar{M}_z$ = 8,22,854. These values are in accordance with the normal molecular weight distribution pattern.[15] GPC gave the polydispersity of PS as 1.588, while the a = 0.778 and
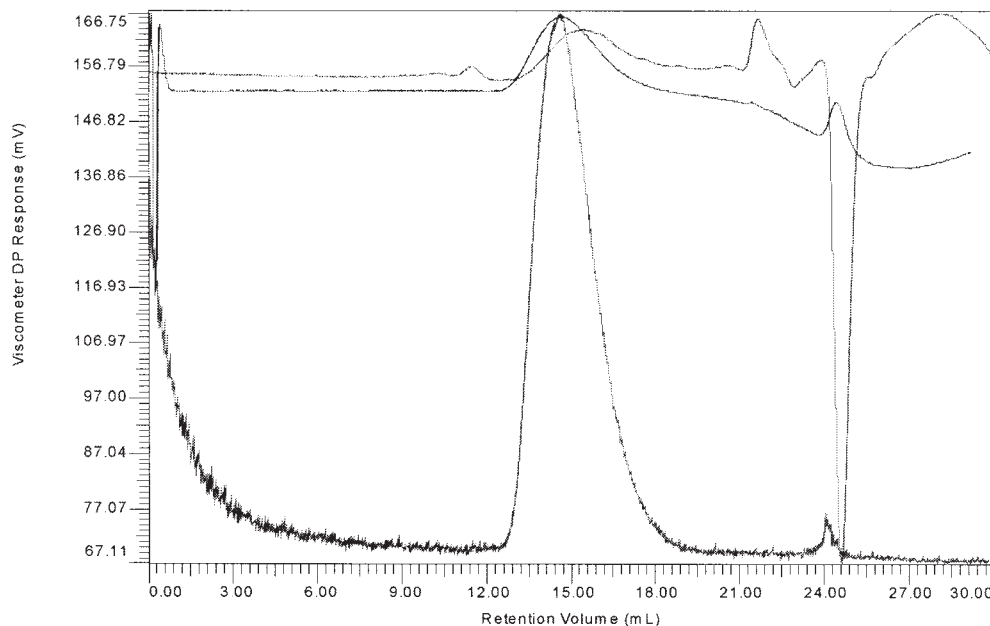
Figure 2 GPC chromatogram of polystyrene.

log $K = -4.286$. These values are in agreement with the literature data.[16]

Molecular weight of PS was also determined from dilute solution viscosity measurements. For this study, PS was dissolved in toluene in five different concentrations (0.2, 0.4, 0.6, 0.8, and 1.0 mass %). Then, by plotting reduced viscosity versus concentration of PS (see Fig. 3), the intrinsic viscosity, $[\eta]$ as obtained from the intercept, was 87.72 dL/g. Molecular weight was calculated using the Mark–Houwink–Sakurada equation[15]

$$[\eta] = K\bar{M}_\eta^a \tag{1}$$

where K and a values are dependent on the polymer and solvent as well as the temperature. Taking these values from the literature,[16] we have calculated viscosity average molecular weight, $\bar{M}_\eta = 2,40,336$ for polystyrene.
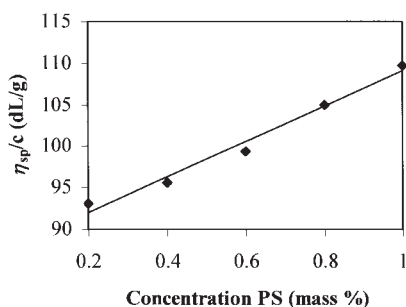

Figure 3 Plot of reduced viscosity versus concentration of polystyrene.

Energy transfer processes in PS solutions

Energy transfer occurs if the excitation energy level of a donor is higher than that of an acceptor during the lifetime of the donor. Excitation transfer probability depends upon the coupling strength of the donor and the acceptor. According to Forster,[17,18] energy is transferred by a dipole-dipole resonance interaction between the donor and the acceptor molecule. Such an interaction varies inversely with the distance between the donor and the acceptor molecules. In the case of singlet energy transfer, "critical transfer radius" for this interaction is typically of the order of 2–10 nm. In some cases, when dipole-dipole transfer of electronic excitation energy is negligible, higher order (multipole) interactions between the donor and the acceptor may become significant. If the probability of multiple interactions is low, then the exchange resonance interaction may prevail.[19] The favorable conditions for this resonance transfer of excitation energy exist if the molecules are in contact, that is, when donor and acceptor molecular orbitals overlap. In the present systems, dipole-dipole interactions are to be considered because of sufficiently high donor and acceptor concentrations and high effective viscosity of the PS solutions.

From the recorded spectra, we observe two absorption and two emission peaks for Exalite in 1,4-dioxane. Absorption peaks in 1,4-dioxane are observed at 229 nm and at 353 nm, while fluorescence peaks are observed at 393 nm and at 413 nm. Assuming a spherical shape, the radius of Exalite, r, was determined to be 5.33 Å by adding the atomic van der Waal's volume of
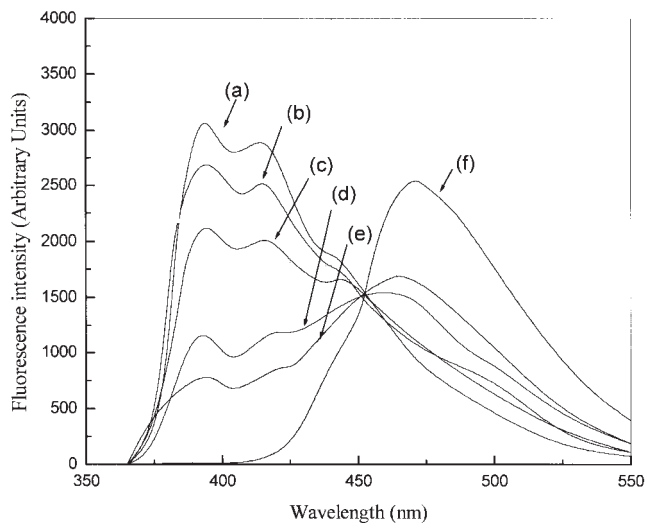
Figure 4 Continuous wave emission spectra of polymer solution system consisting of donor Exalite 416 and acceptor Coumarin 515 dissolved in PS solution of concentration 2.5 g/dL when excited at 353 nm, the excitation wavelength of Exalite, for six different concentrations of Coumarin: (a) 13.3 μM, (b) 16.6 μM, (c) 20 μM, (d) 26.2 μM, (e) 30 μM, and (f) 33.3 μM of Coumarin 515 and fixed concentration of Exalite (10^{-4} M).

all the atoms constituting the molecule.[20] Similarly, for Coumarin, peak absorption in 1,4-dioxane is observed at 403 nm, while the fluorescence peak appears at 472 nm. Assuming the spherical shape and by adding atomic van der Waal's volume of all atoms,[20] the radius, r, of Coumarin was calculated to be 4.26 Å. Thus, as required for a good scintillator system, the emission spectrum of the donor dye, Exalite, matches with the absorption spectrum of the acceptor dye, Coumarin.

The energy transfer from donor to accepter should be nonradiative to shorten the fluorescent decay times. To understand the energy transfer from donor to accepter, fluorescence spectra of PS plus two dopants are recorded for different concentrations of Coumarin ranging from 13.3 μM to 33.3 μM, with the fixed Exalite concentration of 10^{-4}M in solution. These spectra are displayed in Figure 4 for six concentrations of Coumarin. From these spectra, the fluorescence intensity for Exalite at 393 nm and for Coumarin at 467 nm are obtained. The variation of fluorescent intensities of the two dopants with the concentration of Coumarin in the system is displayed in Figure 5. It is observed that with increasing concentration of Coumarin, the fluorescent intensity of Exalite decreases linearly while that of Coumarin increases linearly. This is because more energy is transferred nonradiatively from Exalite to Coumarin with increasing concentration of Coumarin. However, some of the fluorescence intensities of the two dopants as a function of the acceptor is not constant; in fact, it decreases. This

means that with increasing concentration of Coumarin, its radiative transition probability decreases.

In an earlier study,[21] from the fluorescent intensity of the acceptor dye DCM at five different concentrations with 10^{-4} M Coumarin-504 in the epoxy polymer matrix, it was found that dye concentration influenced significantly both the decay times and the quantum efficiency. To decrease fluorescence decay time, energy transfer from donor to acceptor should be nonradiative. For a given donor concentration, the higher the acceptor concentration, not only the decay time will be shorter, but quantum efficiency will be higher. However, such a rule does not seem to exist for different concentrations of the donor dye when the acceptor concentration is the same. Thus, our present results are in agreement with the published reports.

The decrease in fluorescence intensity of Exalite with increasing concentration of Coumarin indicates that the fluorescence of Exalite is being quenched by Coumarin. Quenching of Exalite fluorescence by Coumarin can be interpreted quantitatively by the Stern–Volmer equation[22]:

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \qquad (2)$$

where I_0 and I are, respectively, the fluorescence intensities of Exalite in PS solutions in the absence and in the presence of the Coumarin of concentration Q; K_{SV} is the Stern–Volmer constant for the quenching process and is given by:
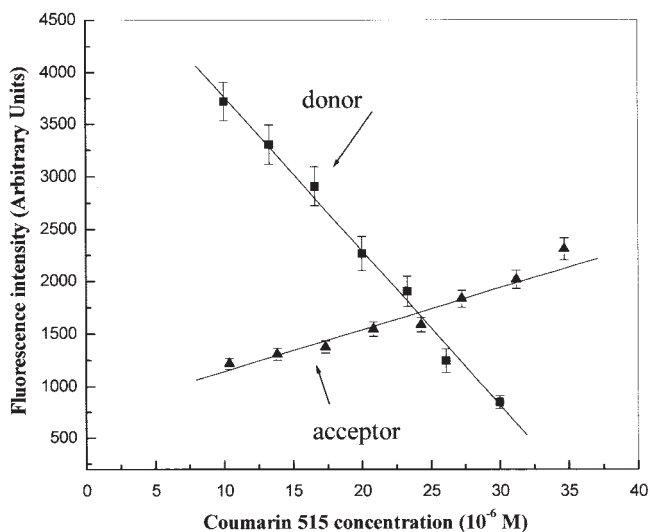
$$K_{SV} = k_q \tau_0 \qquad (3)$$

Figure 5 Variation of the fluorescent intensity of donor Exalite 416 at 393 nm and acceptor Coumarin 515 at 467 nm as a function of Coumarin concentration in PS solution consisting of Exalite and Coumarin when excited at 353 nm, the excitation wavelength of Exalite.
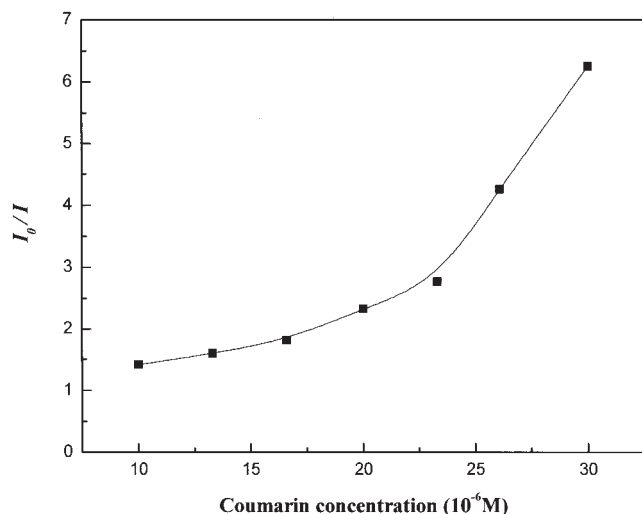
Figure 6 Stern–Volmer plot for quenching of the fluorescence intensity of Exalite by Coumarin.

where k_q is the quenching rate parameter and τ_0 is the lifetime of the donor in the absence of the accepter. It is seen that a plot of I_0/I versus Coumarin concentration would be a straight line with a slope equal to K_{SV} and would yield k_q if τ_0 is known.

The Stern–Volmer plot in the present system shown in Figure 6 is linear at a lower concentration of Coumarin with positive deviation from linearity for higher concentrations. The slope of the linear part of the curve gives the value of K_{SV} equal to (0.060 ± 0.004) 10^6 M^{-1}. From this, k_q the quenching rate parameter for Coumarin in PS solution could not be obtained in the absence of the value of τ_0 for the present environment. However, the positive deviation from linearity at higher concentrations of the accepter dye is due to static fluorescence quenching. Positive deviations from the Stern–Volmer plot may be due to static quenching, which can be explained either due to the ground state complex formation or the sphere of action static quenching models. In the case of the ground state complex formation model,[23] we get the following relationship for the fractional decrease in fluorescence intensity, F, per unit concentration of the quencher:

$$F = \frac{[(I_0/I) - 1)]}{[Q]} = (K_{SV} + k_g) + K_{SV}k_g[Q] \quad (4)$$

Here, k_g is the ground state association constant for the pair of donor and accepter. Here again, the plot of F versus $[Q]$ would be a straight line. However, our data do not yield a straight line and hence, there does not seem to be any formation of the ground state complex of Exalite and Coumarin. Based on the "sphere of action" static quenching model,[24] we can write:

$$\frac{[1 - (I/I_0)]}{[Q]} = K_{SV}(I/I_0) + \frac{(1 - W)}{[Q]} \quad (5)$$

Thus, the plot of $[1-(I/I_0)]/[Q]$ versus I/I_0 would be linear, but our data do not yield a linear plot, indicating that this model is also not adequate to explain the results.

CONCLUSION

The polystyrene used in this study was prepared by emulsion polymerization and was fully characterized by gel permeation chromatography, viscosity measurements, and differential scanning calorimetry. Energy transfer processes are found to be in wavelength shifters, including both radiative and nonradiative processes. Nonradiative energy transfer of the electronic excitation energy may be due to dipole-dipole or higher order (multiple) interactions between the donor and the acceptor. However, the energy transfer from donor to accepter should be nonradiative to achieve shorter fluorescent decay times. To optimize the light output and to obtain short decay times, emission spectra of the individual dyes as dopants in the polystyrene solution have been studied as a function of concentration. Results of this study have shown that the relative intensities change with concentrations. Fluorescent intensity of Coumarin increased linearly with its concentration. This is because more energy is transferred nonradiatively to Coumarin from Exalite. The Stern–Volmer constant for quenching of fluorescence of Exalite by Coumarin is obtained, and a positive deviation from the Stern–Volmer relation has been observed.

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