Spectrophotometric Investigation of Laser Dye Diffusion in Styrene–Acrylonitrile Copolymer Solutions

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ABSTRACT: An ultraviolet spectrometer was used to measure the absorption kinetics of a laser dye, 1,4-bis(5-phenyloxazoyl-2-yl) benzene, at its maximum wavelength in solutions of styrene–acrylonitrile copolymer dissolved in 1,4-dioxane. From the time-dependent absorbance data, the dye diffusion coefficient was calculated by a combination of Fick's law of diffusion with the Beer–Lambert law of absorption. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1481–1484, 2005

Key words: diffusion; solution properties; dyes/pigments

INTRODUCTION

In earlier studies, we spectrophotometrically investigated the diffusion of scintillating dyes in polystyrene and poly(methyl methacrylate) solutions.[1,2] In continuation of this research, in this study, we examined the diffusion of a laser dye, 1,4-bis(5-phenyloxazoyl-2-yl) benzene (POPOP), in styrene–acrylonitrile (SAN) copolymer dissolved in 1,4-dioxane at different concentrations of the dye and the copolymer. The spectrophotometer was used to record the absorption spectra of the POPOP diffusing in the SAN solution in a standard cuvette. From the recorded spectra, the solute concentration was determined as a function of time. These data were used to compute the dye diffusion coefficient (*D*) of POPOP in SAN polymer solutions of different concentrations at 30°C. The concentration dependence of dye diffusion in the SAN solutions was studied.

EXPERIMENTAL

Materials

Scintillating-grade POPOP dye was obtained from S. D. Fine Chemicals (Mumbai, India). Analytical-grade 1,4-dioxane was also purchased from S. D. Fine Chemicals. The SAN copolymer was received as a gift sample from CIPET (Mysore, India). The experimental setup consisted of a diffusion cell, which was a rectangular quartz cell 45 mm in height and with 10-mm sides. The heights of the polymer solution and the dye solution were 30 and 10 mm, respectively.

PREPARATION OF THE SAN COPOLYMER AND POPOP SOLUTIONS

The SAN copolymer and POPOP were weighed in an electronic Mettler balance (model AE 240, Greifensee, Switzerland) accurate to ±0.01 mg. Different concentrations (0.5, 1.0, 1.5, 2.0, 2.5, and 3×10^{-3} *M*) of POPOP dye solutions were prepared by the dissolution of the required amounts of POPOP in 1,4-dioxane. SAN copolymer solutions with concentrations of 5, 7.5, and 10 g/dL were prepared by mass in 1,4-dioxane.

Diffusion cell

The diffusion cell was prepared by the addition of 3 mL of polymer solution to an ultraviolet quartz cu-
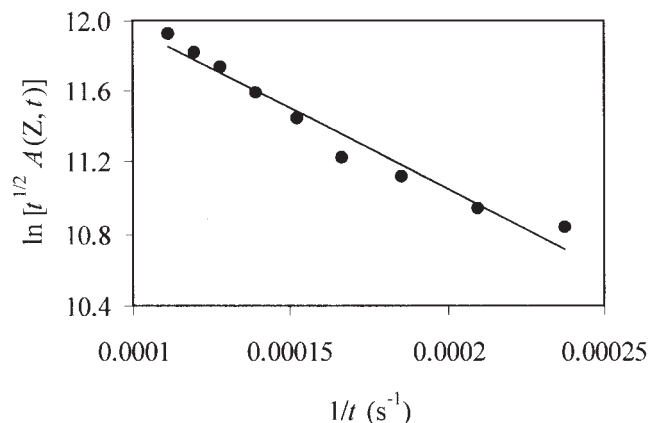
Figure 1 Variation of $\ln[\sqrt{t}A(Z,t)]$ with $1/t$ for POPOP (2×10^{-3} M) diffusing in a 7.5-g/dL SAN copolymer solution at different time intervals (t) after the commencement of diffusion at 30°C.

vette placed in the sample compartment of the spectrophotometer. The sample was stabilized at 30°C for 10–15 min. Then, 1 mL of the POPOP solution prepared in 1,4-dioxane was gently introduced from the top of the SAN solution through a small glass funnel having a capillary tube and positioned at the corner of the cell (see our earlier article[1] for this experimental setup). The POPOP solution, being lighter than the SAN solution, formed a colored band above the colorless transparent SAN solution. The temperature of the diffusion cell was controlled within ±0.1°C with a temperature-controlled unit attached to the ultraviolet spectrophotometer (Anthelie, Secomam, France). The absorbance [$A(Z,t)$] (Z is the horizontal plane distance from the interface) accuracy was ±0.0004, and the wavelength accuracy was ±0.2 nm. Spectra were scanned at 30°C.

RESULTS AND DISCUSSION

The absorption peak of POPOP was observed at 360 nm, which was rather widely separated from the absorption peak of 1,4-dioxane at 210 nm and that of SAN at 276 nm[3]. Because we were interested in the diffusion of POPOP in the SAN solution, the range of wavelengths was chosen as 300–400 nm, which was the absorption region for POPOP. Just before the POPOP solution was introduced over the SAN solution, the recorded spectrum produced a flat baseline. After the introduction of the POPOP solution, the absorption spectrum of POPOP, observed as a broad peak at 360 nm, steadily increased with time, indicating an increase in the concentration of POPOP because of its progressive diffusion.

D was computed from the combined application of Fick's law of diffusion[4] and the Beer–Lambert law.

Fick's law gives the relationship between $C(Z,t)$ (where t is time) and D, whereas the Beer–Lambert law is used to calculate concentration, $C(Z,t)$ in terms of $A(Z,t)$. According to Fick's second law of diffusion, along the z axis, we have[4]

$$\left(\frac{\partial C}{\partial t}\right)_z = D\left(\frac{\partial^2 C}{\partial z^2}\right)_t \tag{1}$$

With appropriate boundary conditions, eq. (1) becomes

$$\ln[\sqrt{t}C(Z,t)] = \ln\left[\frac{C_0}{\sqrt{\pi D}}\right] = \left[\frac{Z^2}{4D}\right]\frac{1}{t} \tag{2}$$

where C_0 is a constant equal to the concentration of the dye per unit area at $Z = 0$ and $t = 0$. Thus, a plot of $\ln[\sqrt{t}C(Z,t)]$ versus $1/t$ is a straight line with a slope of $(Z^2/4D)$. From the values of $C(Z,t)$ measured as a function of time, D was calculated by the measurement of $A(Z,t)$ corresponding to $C(Z,t)$.

According to the Beer–Lambert law, the transmitted intensity, related to incident intensity and concentration [$C(Z,t)$], is given by

$$C(Z,t) = \frac{2,303}{\varepsilon L}A(Z,t) \tag{3}$$

where ε is the molar extinction coefficient of the dye and L is the path length. If we combine eqs. (2) and (3), we get

$$\ln[\sqrt{t}A(Z,t)] = \ln\left[\frac{C_0\varepsilon L}{2.303\sqrt{\pi D}}\right] - \left(\frac{Z^2}{4D}\right)\frac{1}{t} \tag{4}$$

Thus, the linear plot of $\ln[\sqrt{t}A(Z,t)]$ versus $1/t$ can be constructed to give a slope of $-(Z^2/4D)$. Thus, from the measured values of $A(Z, t)$ at known t values, D can be calculated.

In this method, we obtained $A(Z,t)$ as a function of time by placing the diffusion cell in a spectrophotometer and then recording the absorption spectra at different intervals. Before introducing the dye solution over the SAN solution, we took the absorption spec-

TABLE I
D Values of POPOP (2×10^{-3} M) in SAN Copolymer Solutions of Different Concentrations at 30°C

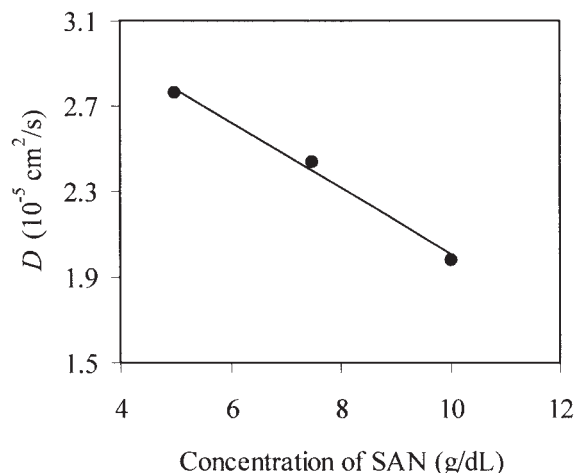| Concentration of the polymer (g/dL)	$D \times 10^5$ (cm²/s)
5.00	2.76
7.50	2.44
10.00	1.98

Figure 2 Variation in the D values of POPOP in SAN copolymer solutions of different concentrations at 30°C.

trum of the SAN solution as the reference spectrum. After the dye solution was introduced over that of the SAN solution, the absorption spectra were automatically scanned and saved at preprogrammed intervals. Because the absorption spectrum of the SAN solution was subtracted from each of the absorption spectra of the dye-containing SAN solution, the recorded spectra represented the absorption spectra of the dye.

The absorption spectra represented the plot of $A(Z,t,\lambda)$ versus wavelength (λ), which had a broad peak. The characteristic wavelength of the absorbing molecule (λ_m) was used to identify the diffusing dye. In eq. (4), $A(Z,t)$ was used at λ_m. From the spectra recorded at different times and with eq. (4), D of POPOP was calculated. The absorption spectra were
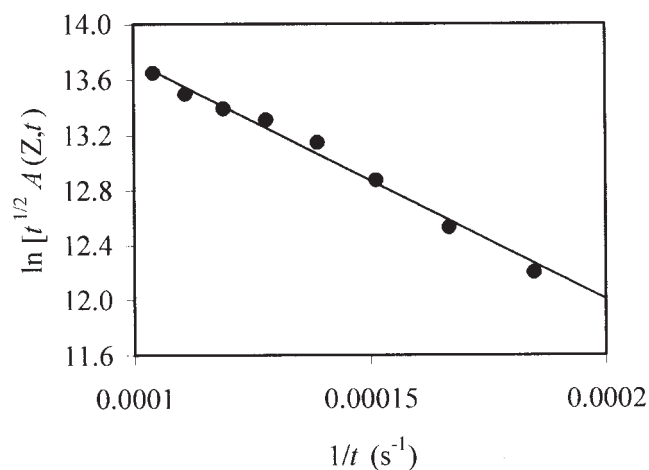

Figure 3 Variation of ln[$\sqrt{t}A(Z,t)$] with $1/t$ for POPOP (1.0 × 10⁻³M) diffusing into a 10-g/dL SAN copolymer solution at different time intervals (t) after the commencement of diffusion at 30°C.

TABLE II
***D* Values of POPOP in SAN Copolymer Solutions at Different Concentrations of POPOP at 30°C**

Concentration of the dye (10^{-3} M)	$D \times 10^5$ (cm²/s)
0.5	1.20
1.0	1.41
1.5	1.67
2.0	1.98
2.5	2.14
3.0	2.35

recorded at intervals of 10 min up to 3 h to study the diffusion of a 2×10^{-3}-M concentration of POPOP at different concentrations (5, 7.5, and 10 g/dL) of the SAN solution. A typical plot of $A(Z,t)$ at 360 nm versus time for a 2×10^{-3}-M POPOP solution diffusing in 7.5-g/dL SAN was used to construct a plot of ln[$\sqrt{t}A(Z,t)$] versus $1/t$ (see Fig. 1). From the slope of the straight line (deviation < 2%), a value of D of $(2.44 \pm 0.02) \times 10^{-5}$ cm²/s was calculated.

The values of D calculated in 5-, 7.5-, and 10-g/dL SAN solutions in 1,4-dioxane are presented in Table I. The results of D varied linearly with the concentration (C) of the polymer solution according to[5]

$$D = D_0(1 + kC) \tag{5}$$

where k is the virial coefficient. The plot of D versus C was a straight line with a maximum deviation of 1.5% (see Fig. 2). The true diffusion coefficient (D_0) in the pure solvent was calculated to be $(3.56 \pm 0.02) \times 10^{-5}$ cm²/s.

When the SAN concentration was kept constant at 10 g/dL, the POPOP concentration varied from 0.5 to 3×10^{-3} M at an interval of 0.5×10^{-3} M. A typical
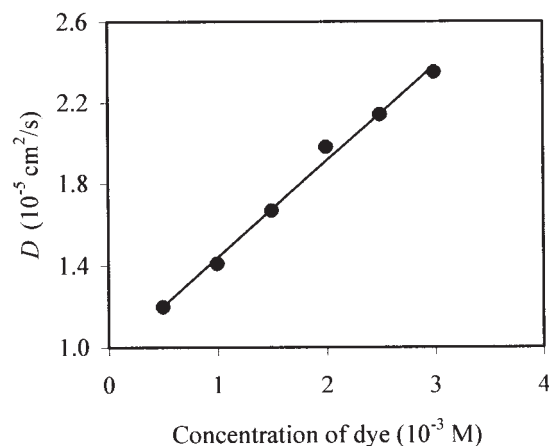

Figure 4 Variation in the D values of POPOP of different concentrations in a 10-g/dL SAN copolymer solution at 30°C.

plot of $\ln[\sqrt{t}A(Z,t)]$ versus $1/t$ for the diffusion of POPOP (1×10^{-3} M) in 10-g/dL polymer solutions is shown in Figure 3. The D value calculated from the slope of the straight line was $(1.41 \pm 0.03) \times 10^{-5}$ cm^2/s. These data are given in Table II. From the plot of D versus C of POPOP shown in Figure 4, it was evident that D varied linearly with concentration.

In conclusion, this method is simple and rapid yet gives reproducible D values of POPOP dye in SAN solutions.

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