

Simultaneous Diffusion of a Disperse Dye and a Solvent in PET Film Analyzed by Rutherford Backscattering Spectrometry

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SYNOPSIS

Poly(ethylene terephthalate) (PET) is a difficult fiber to dye from an aqueous dyebath due to its high degree of crystallinity and lack of polar groups. One method used to increase the dyeing rate of the fibers is the addition of an organic solvent, called a dye carrier, to the aqueous bath. This study utilized Rutherford backscattering spectrometry and neutron activation analysis to examine both simultaneous diffusion and individual diffusion characteristics of a disperse dye and a dye carrier into PET film. The dye exhibited Fickian diffusion above and below glass transition temperature (T_g) of the PET film both in the presence and absence of solvent. The presence of carrier in the dyebath was found to increase the diffusion coefficient of the dye at each temperature condition; increasing from 10^{-14} to 10^{-11} cm²/s below T_g (65°C) and 10^{-12} to 10^{-10} cm²/s above T_g (90°C). Bromobenzene exhibited case II diffusion below T_g of the film, which indicates that the solvent is swelling the near surface regions of the film. This increase in void volume resulted in an increased dye uptake when films dyed in the presence of carrier were compared with those dyed without carrier. In fact, the penetration depth of the dye was found to be equivalent to that of the swollen region of the film (~ 600 nm) after 15 s. Above T_g , the bromobenzene exhibited Fickian diffusion. The coupling of the increased thermal motion of the polymer at the higher temperature and the solvent effect increased dye uptake when compared either with dye uptake at the lower temperature or with uptake when no solvent was present. The application of the dye and solvent simultaneously did not affect the diffusion mechanism of either species, leading to the conclusion that there was no competition for specific sites between these two species in the PET film. Similar results were obtained for chlorobenzene when used as the dye carrier. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The most common form of polyester, poly(ethylene terephthalate) (PET), in its unmodified form, is difficult to dye from an aqueous dyebath since it absorbs only 0.4% water and does not swell in water.¹ This lack of interaction between the polyester and the dyebath requires that disperse dyes and either high temperature/high pressure systems or dyebaths containing organic solvents called dye carriers be used in order to increase the rate of dye uptake to an industrially acceptable level.

Much work has been done in the last 30 years in an attempt to understand the mechanisms by which the carriers function in the dyebath. It is generally accepted that they decrease the glass transition temperature (T_g) of the polyester, allowing dyeing to take place at lower temperatures and faster rates than would otherwise be achievable. The majority of past research has concentrated on either the carrier effects on physical properties of the fibers or the changes in the dyeability of the fibers with the addition of a carrier to the dyebath.²⁻⁵ Due to limitations in available analytical technology, little research has examined the simultaneous diffusion of the dye and carrier. Most of the previous work has relied on the visibility of the dye front in the determination of diffusion mechanisms and rates. The

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carrier, which does not provide a colored diffusion front, presents a problem when using this methodology.

In an attempt to elucidate the mechanism by which some select dye carriers function, our previous research used Rutherford backscattering spectrometry (RBS) to investigate the diffusion of disperse dye in the presence of two dye carriers in polyester films.⁶ This technique relies not on the visibility of the colored dye front but on the presence of an elemental tag for the profiling of the diffusion front of a species. The purpose of the present study is to use the RBS technique to observe and quantify the diffusion parameters of a dye and solvent in PET film and examine the effect of the simultaneous diffusion of the two species on their individual diffusion profiles. The method is supplemented by data from neutron activation analysis and depth of shade measurements. The data were analyzed relative to common diffusion models in order to determine the diffusion parameters of each of the species when applied alone and simultaneously from an aqueous bath.

EXPERIMENTAL METHODS

Materials

The dye used was Polycron Orange 5R (Disperse Orange 5) ($C_{15}H_{14}Cl_2N_4O_3$) provided by Atlantic Industries, Inc., Nutley, NJ. The solvents (dye carriers) were bromobenzene, 99% (C_6H_5Br), supplied by Aldrich Chemical Company, Inc., Milwaukee, WI; and chlorobenzene (C_6H_5Cl) supplied by Mallinckrodt, Inc., Paris, KY. The PET substrate was 92-gauge (25- μ m-thick), Type A Mylar film supplied by E. I. DuPont de Nemours & Company, Inc., Wilmington, DE. The film was uncoated, with no surface treatment and a surface roughness of 38 nm.⁷ Differential scanning calorimetry revealed the crystallinity of the film to be approximately 40% and T_g to be approximately 76°C.

Theory of RBS

RBS is a technique which allows depth profiling of heavy elements in films, down to a depth of a few micrometers.⁸ A light ion beam (typically $^4He^{2+}$) is impinged upon a flat sample surface. As incident ions collide with nuclei of atoms in the sample, they are backscattered into an energy-sensitive detector with an energy that is dependent on both the mass of the target atom and its depth from the sample surface. A spectrum of the number of backscattered

ions versus their energy is produced, providing a depth profile of the elements present in the sample. From the resulting depth profile, diffusion characteristics of the diffusants present in the sample can be determined. In our study, RBS was used to determine diffusion parameters of the dye and carrier in the PET film at the initial stages of the dyeing process. The bromine present in the solvent molecule (bromobenzene) and chlorine present in the dye molecule (Disperse Orange 5) and in chlorobenzene were the target atoms for the RBS analyses.

Sample Preparation for RBS

PET film samples (1.5 cm \times 3 cm) were cleaned at room temperature by soaking in acetone (8 h); drying (6 h); soaking in deionized, distilled water (8 h); and drying (6 h). Hardman Extra-Fast Setting EpoxyTM was then used to attach each specimen to a thin 2.25-cm² aluminum substrate such that a tail of film extended beyond the edge of the aluminum. A thin copper wire was then strung through the extending film tail to allow for easy insertion and removal of the PET specimens from the treatment baths.

A three-necked round-bottom flask fitted with a condenser tube, the temperature probe of a WhatmanTM programmable hotplate, and a rubber stopper, through the neck of which samples were introduced to and removed from the bath, served as the dyeing vessel. A stirring rate of 200 revolutions per minute was used.

Three treatment baths were used: 50 mL of deionized, distilled water and 0.1 g of disperse dye; 50 mL water and 0.25 g of bromo- or chlorobenzene; and 50 mL water, 0.1 g disperse dye, and 0.25 g bromobenzene. Samples were immersed in the baths when an equilibrium temperature of 65°C or 90°C was reached. These temperatures were chosen as they represented temperatures below and above T_g of the polyester film (\sim 76°C). Immersion times at the two temperatures were as follows: dye only –90 min at 65°C, and 5, 10, and 30 min at 90°C; bromo- or chlorobenzene only –5, 10, and 15 s at both 65°C and 90°C; dye and bromobenzene –2, 5, and 10 s at 65°C, and 5 and 10 s at 90°C. The short exposure times were necessary to prevent overlapping of the bromine and chlorine depth profiles with each other and/or with the peak produced by surface oxygen in the RBS spectra. Three replicates of each treatment condition were prepared from different dye-baths, but each set of exposure times was carried out from the same bath. One sample each of 30-, 60-, and 120-s exposure time for the bromobenzene at 65°C was run to determine diffusion parameters at longer time exposures.

Following treatment, samples were removed from the treatment bath and immediately immersed in liquid nitrogen to prevent changes in the diffusion profile of the dye and/or carrier before RBS measurements. Samples were not rinsed to remove surface dye because rinsing would affect the diffusion profile of the bromobenzene.

RBS spectra were obtained using a $^4\text{He}^{2+}$ beam with an energy of 2.7 MeV. The sample chamber was cooled to liquid nitrogen temperature before analysis to prevent diffusion of the dye and/or carrier during the analysis.

Minitab^{TM,9} a statistical software package, was used to calculate ANOVAs and Tukey's multiple means comparison tests to determine the statistical significance of results. All statistics are reported at the 95% confidence level.

Theory of Neutron Activation Analysis

Neutron Activation Analysis (NAA) is a bulk gamma-ray spectrometry technique that can be used to determine trace quantities of elements in a substrate.¹⁰ It was used in this study to determine the amounts of the dye and solvent after longer treatment times (greater diffusion depths) than could be profiled by RBS.

NAA involves exposing a sample to a neutron flux in a nuclear reactor.¹⁰ As the sample is irradiated, neutrons are absorbed by the target atomic nuclei. Some of the excess energy produced in the sample is immediately released as gamma radiation. Since each element produces gamma radiation of characteristic energies in quantities proportional to the number of atoms of that element that are present, gamma-ray spectrometry allows for trace elemental analysis within a solid sample. Following exposure to the neutron flux, the sample is transferred to a detector that measures the number of gamma rays produced at a given energy.

Sample Preparation for NAA

Samples (1.5 cm \times 3 cm) were cleaned in the same manner as those used for RBS. Following cleaning, each sample was weighed to the nearest ± 0.01 g before being mounted on an aluminum substrate and attached to the copper wire.

To produce uptake curves, samples were treated for the following times at each temperature (65°C or 90°C): dye only 5, 10, 30, 60, and 120 min; carrier only and dye and carrier 5, 10, and 15 s and 1, 10, 30, and 60 min. Following treatment, samples were blotted dry without being rinsed and were stored in individual plastic bags in a freezer. They were

transported to the Ward Laboratory nuclear reactor facility at Cornell University in a liquid nitrogen Dewar and transferred to a 2/27-dram polyethylene vial. Seven vials were placed into a TeflonTM holder for each run. The holder was then inserted into a large polyethylene vial, on the bottom of which was a small aluminum-gold wire standard that was used to monitor the neutron flux. A long string, attached to the cap of the large vial, allowed for its introduction and removal from a position near the reactor core. The large polyethylene vial was inserted into a dry tube of the TrigaTM research reactor for 10 min at 300 kW. Following exposure, it was removed from the reactor and each individual sample was transferred to a clean vial for counting. Depending on the intensity of the resulting gamma signal, counting was carried out for 10 min at a position either next to or 10 cm from the high-purity germanium solid-state detector window. The signal was processed through an analog-to-digital converter and displayed on a multichannel analyzer.

Following counting, the areas under the peaks characteristic for bromine (776 keV) and chlorine (1642 keV) were integrated for total counts. Counts per second were adjusted for flux variations, converted to the number of chlorine and/or bromine atoms and then converted to a dye/solvent concentration (g/cm³).

Dye Uptake

Dye uptake experiments were carried out on polyester fabrics supplied by Testfabrics, Inc., Middlesex, NJ, to determine the effect of the carrier on the resulting depth of shade obtained under fiber dyeing conditions. Fabrics cut into 36 cm² swatches were washed at 40°C for 10 min in a 0.02% nonionic detergent solution using a Terg-o-TometerTM. They were rinsed three times in distilled water using a BurrelTM shaker and allowed to dry at room temperature before dyeing.

Dyeing was carried out at 65°C and 90°C for 1, 2, and 3 h. The dyeing apparatus consisted of a 1000-mL three-neck flask set up in the same manner as for the RBS and NAA experiments. The dyebath consisted of 500 mL distilled water, 0.1 g dye [6% of fabric weight (owf)] and, for carrier treated samples, 0.25 g carrier (15% owf). Three fabric swatches were dyed in each bath (total weight \sim 1.7 g). After dyeing, surface dye was removed from each swatch by rinsing in acetone until the rinsate was visually clear (about 3 times).

Color differences between samples dyed with and without carrier for 1, 2, and 3 h were measured using a MacBethTM Color Eye with a 10° observer and a

D₆₅ illuminant (daylight). K/S values, which indicate the relative lightness or darkness of one sample compared to another (the higher the K/S value, the darker the sample), were determined in percentage of apparent strength over the visible region of the spectrum (400–700 nm). A washed, undyed fabric swatch was used as the standard. K/S values with the value for the standard subtracted were determined at three locations on each sample.

RESULTS AND DISCUSSION

Effect of Temperature

This portion of the study examined the diffusion of the dye and bromobenzene above and below the T_g of the PET film to determine whether competition for specific sites in the polymer was occurring when the two species were applied simultaneously.

Bromobenzene Diffusion Below T_g (65°C)

In the RBS spectrum obtained for bromobenzene [Fig. 1(a)], the signal from the surface bromine is seen at ~ 2.3 MeV, and progressive depths are shown to 1.1 MeV where scattering energies appear due to surface oxygen. The greater the intensity, or height of the signal, the more abundant the atom.

Based upon the RBS results, the bromobenzene diffusion in PET does not follow classical Fickian diffusion. The depth profile of bromine consisted of two regions: a region of constant concentration near the surface followed by a region with an exponential decrease in concentration (Fig. 2). This type of diffusion profile characterizes case II diffusion and has been observed by other authors studying the diffusion of solvents into glassy polymers and semicrystalline polymers below their T_g .^{3,11–13} Case II diffusion is the result of a buildup of the solvent fraction at the surface of the polymer that, after reaching a critical value, forms a front which advances into the polymer at a constant velocity.^{11,14} The front buildup is due to two competing forces: the osmotic pressure, which arises due to the solvent concentration difference between the inside and the outside of the substrate and favors inward diffusion of the solvent; and internal stresses, which arise due to the resistance of the polymer to swelling and retard solvent diffusion.¹⁴

The characteristics of the solvent diffusion can be determined by breaking the profile into regions and solving the diffusion equation describing each region. The solution for the Fickian precursor ahead of the front when the diffusion coefficient is not a

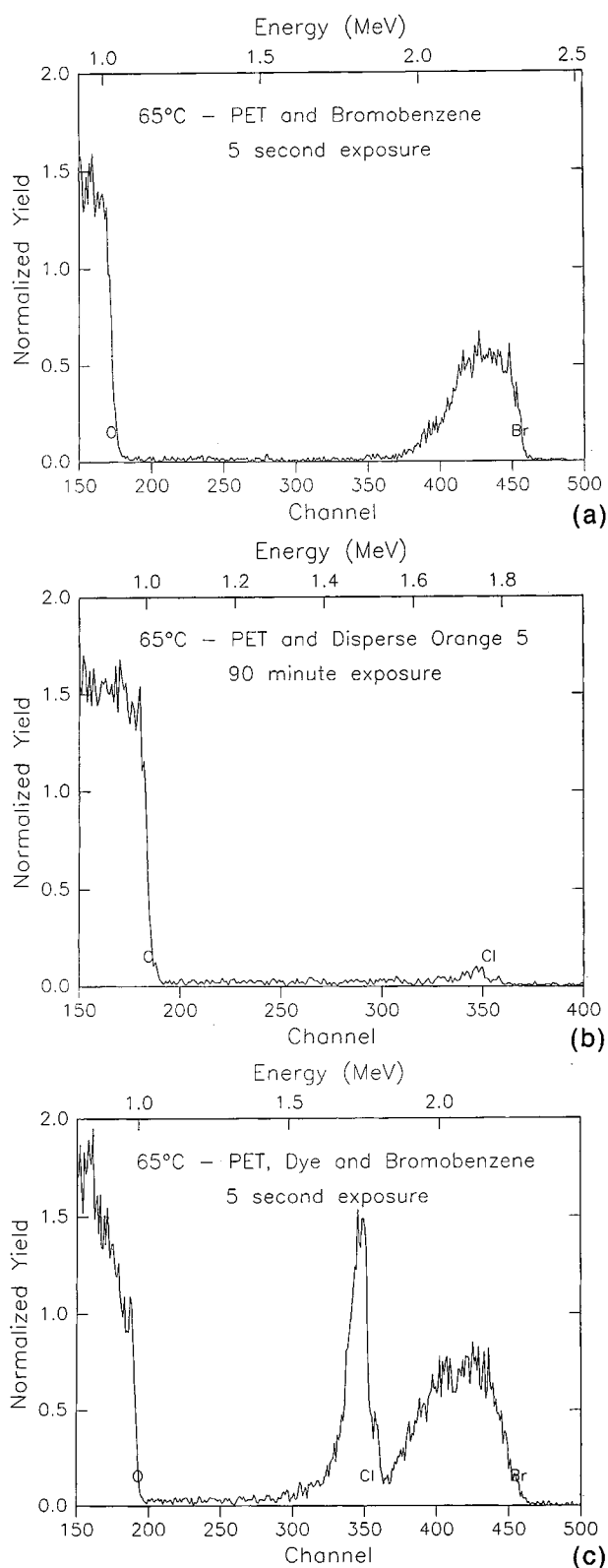


Figure 1 Typical RBS spectra at 65°C for (a) bromobenzene diffusion in PET film after 5 s exposure, (b) dye diffusion in PET film after 90 min exposure, and (c) dye and solvent applied simultaneously to PET film after 5 s exposure.

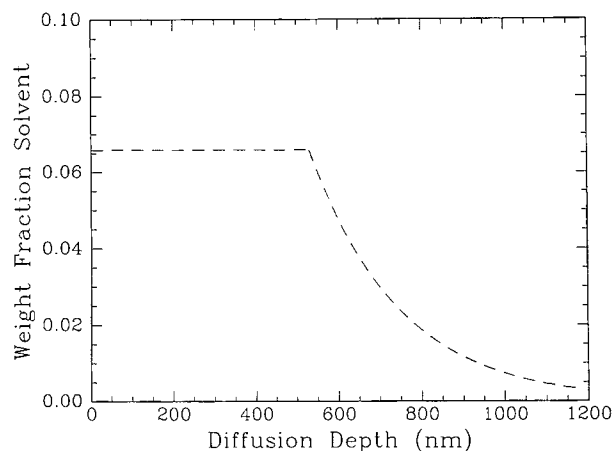


Figure 2 RBS spectrum for bromobenzene diffusion in PET film [Fig. 1 (a)] converted to weight fraction versus diffusion depth.

function of solvent concentration can be expressed as

$$\phi = \phi_c \left(\exp \frac{-x}{D/V} \right) \quad (1)$$

where ϕ is the fraction of solvent at a distance x in the film, ϕ_c is the critical solvent fraction necessary for the case II front to form, D is the diffusion coefficient, x is the diffusion distance ahead of the front, and V is the front velocity.^{11,14}

To determine the velocity of the bromobenzene diffusion front, the front depth is plotted versus the exposure time.¹¹ The slope of the resulting straight line is the front velocity (V). Once the front velocity is determined, the diffusion coefficient (D) and crit-

ical solvent fraction (ϕ_c) can be determined using computer simulation to solve eq. (1).¹⁵ The critical solvent fraction for case II diffusion, ϕ_c , is then converted to a weight fraction, ϕ_w . The concentration of solvent in the PET (g/cm^3) can then be determined by integrating under the constant and exponential regions of the diffusion profile and multiplying by the density of the PET film [$\rho = 1.39 \text{ g}/\text{cm}^3$ (ref. 7)] divided by its thickness [$l = 0.0025 \text{ cm}$ (ref. 7)] as follows:

$$\text{Weight/Volume (g/cm}^3\text{)} = \frac{\rho}{l} \left[\int_0^{x_f} \phi_w dx + \int_{x_f}^{\infty} \phi_w \exp \frac{-x}{D/V} \right] \quad (2)$$

where ϕ_w is the weight fraction of solvent in the constant region, and x_f is the case II front depth, i.e., the depth of constant concentration.

The results of the RBS analysis for diffusion of bromobenzene into PET film at 65°C are shown in Table I, where the r^2 value for front velocity is the fit for the front depth versus exposure time. Case II diffusion assumes the presence of a diffusion front of constant concentration which advances at a constant velocity.^{11,14} Once the front forms, solvent moves rapidly toward the glassy region of polymer but the fraction of solvent at the surface of the polymer is constrained due to the slow motion of polymer chains. However, with time, the polymer “yields” due to the high osmotic pressure of the solvent. Thus, whereas the solvent concentration at the surface of the polymer can be viewed as constant with time after front formation, the diffusion coefficient increases with time due to increasing polymer mo-

Table I Bromobenzene Diffusion Parameters in PET Film at 65°C

Exposure Time	Front Depth (nm)	Total Diffusion Depth (nm)	Front Velocity (nm/s) $r^2 = 0.963$	Diffusion Coefficient ($10^{-11} \text{ cm}^2/\text{s}$)	Solvent Weight Fraction at PET Surface	Average Solvent Concentration in Film ($10^{-3} \text{ g}/\text{cm}^3$)	
						RBS	NAA
5 s	482 (40)	1308 (94)	6.10	1.6 (0.2)	0.06 (0.01)	1.5 (0.28)	1.0 (0.4)
10 s	483 (29)	1483 (29)	6.10	3.0 (0.2)	0.07 (0.004)	2.4 (0.18)	2.0 (1.1)
15 s	625 (119)	2150 (617)	6.10	3.6 (1.5)	0.06 (0.04)	2.5 (1.1)	2.9 (2.1)
30 s	680	1680	6.10	3.2	0.03	2.7	
60 s	900	2700	6.10	6.1	0.05	3.4	5.3 (3.7)
120 s	1200	3100	6.10	24.3	0.08	9.2	
10 min							12 (8.0)
30 min							18 (2.3)
60 min							13 (3.5)

Average (standard deviation).

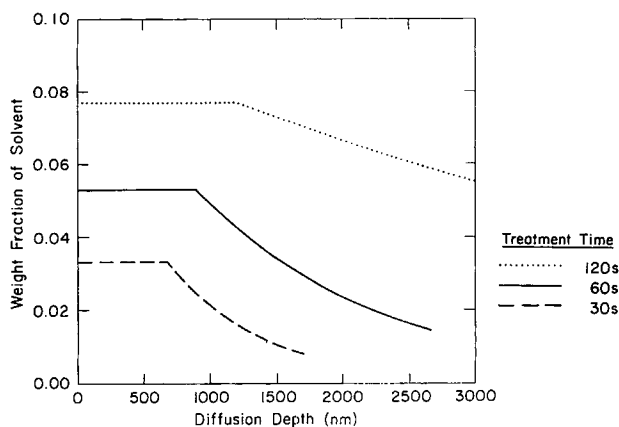


Figure 3 Weight fraction versus diffusion depth for bromobenzene diffusion in PET film at 65°C for (---) 30 s, (—) 60 s, and (····) 120 s. The plot illustrates the increasing case II front depth and nearly constant surface weight fraction with time.

bility. These factors are illustrated in Table I and Figure 3. While the differences between solvent surface concentrations in Figure 3 appear significant; note that the y axis scale is very small. These differences were found to be on the same order as those observed by other authors.¹²

The amount of bromobenzene measured by NAA was not significantly different from the RBS-measured values for the 5-, 10-, 15-, and 60-s exposure times (Table I). The use of the NAA technique allowed us to observe the carrier concentrations over a wider range of treatment times than the RBS. It was found that the carrier concentration did not increase significantly after 10 min.

Below T_g , we found that the bromobenzene (carrier) exhibited case II diffusion profiles both in the

presence and absence of the dye [Fig. 1(a,c)]. Bilovits and Durning³ found case II diffusion in PET after treatment with mild (acetone) and strong (dimethylformamide) swelling agents for PET at temperatures below T_g but not with methanol, a weak swelling agent for PET. Needles and Walker¹⁶ found that bromobenzene had a mild interaction with PET; thus, case II diffusion would be expected.

Dye Diffusion Below T_g (65°C)

The dye uptake was found to be very low in the absence of carrier, and it was difficult to obtain a good RBS profile. Therefore, diffusion was observed after only one dyeing time (90 min) for PET film treated with dye only [Fig. 1(b)]. Surface chlorine present in the dye appears at ~ 1.9 MeV in the RBS spectrum. With no carrier at 65°C for 90 min, the dye diffusion depth was 400 nm and the diffusion coefficient was 0.0023×10^{-11} cm²/s.

Since the sensitivity of NAA allows for the detection of very small amounts of any element in a substrate, dye concentrations in the PET film could be determined for exposure times shorter than the 90 min used for RBS. When dyeing PET without carrier at 65°C, the dye concentration was higher for samples dyed for 10 min than those dyed for 5 min (Table II). After 10 min the dye concentration in the film did not increase significantly with further time.

The dye was found to diffuse in a Fickian manner [Fig. 1(b)]. The very slow rate of uptake was expected as it is a much larger molecule than the bromobenzene (the molecular weight being 369.14 g/mol as compared to 156.95 g/mol for the bromobenzene). With the treatment temperature below the

Table II Amount of Dye in PET Film After Varying Treatment Times Determined by Neutron Activation Analysis

Exposure Time	Dye Concentration (10 ⁻³ g/cm ³) 65°C		Dye Concentration (10 ⁻³ g/cm ³) 90°C	
	Without Bromobenzene	With Bromobenzene	Without Bromobenzene	With Bromobenzene
5 s		9.2 (7)		1.7 (1)
10 s		9.3 (5)		1.5 (1)
15 s				1.1 (0.3)
1 min		9.4 (2)		1.8 (0.7)
5 min	0.35 (0.01)		1.7 (0.1)	
10 min	0.42 (0.10)	9.4 (2)	2.1 (0.3)	3.4 (1)
30 min	0.50 (0.06)	10.0 (3)	3.6 (0.6)	4.4 (1)
60 min	0.56 (0.09)	8.4 (2)	4.3 (0.9)	5.6 (1)
120 min	0.63 (0.09)		5.6 (0.4)	

Average (standard deviation).

T_g of the PET, the diffusion of a large dye molecule is more affected by the low thermal motion of the polymer chains than is the smaller bromobenzene molecule.

Simultaneous Dye and Bromobenzene Diffusion Below T_g (65°C)

RBS allowed the diffusion profiles of both the dye and carrier to be observed after simultaneous diffusion [Fig. 1(c)]. Again, the carrier exhibited a diffusion profile characteristic of case II diffusion, and the dye exhibited Fickian diffusion which was modeled using an error function. The results are shown in Table III.

In the case of the dye, RBS diffusion profiles showed a sharp dye peak near the surface of the film, and it is of interest to note that the total diffusion distance of the dye applied in the presence of the carrier is approximately the same as the front depth of the solvent (Table III). The RBS and NAA results showed large variability in dye concentration (Table III). This is probably due to the fact that the specimens were not rinsed free of surface dye before analysis. Higher dye concentration values were obtained from NAA than from RBS. NAA showed that the dye concentrations at 65°C were much greater for equivalent time exposures when carrier was present in the bath, compared with the case of no carrier (Table II). The effect of the addition of carrier to the dyebath can also be seen in the increase in the diffusion coefficient of the dye (without carrier, $0.0023 \times 10^{-11} \text{ cm}^2/\text{s}$ versus with carrier, $1.7 \times 10^{-11} \text{ cm}^2/\text{s}$, Table III) and the depth of shade [Fig. 4(a)].

In the case of the bromobenzene, RBS results showed a significant increase in the solvent concentration and total diffusion depth when the exposure time increased from 2 to 10 s (Table III). The front depth was significantly greater after 5 and 10 s than after 2 s, and the diffusion coefficient was found to be higher after 10 s exposure than after 2 and 5 s. When compared with the results obtained when the carrier was applied independently of the dye, the presence of the dye did not significantly change the diffusion parameters of the bromobenzene (Tables I and III).

When the carrier is present, the dye diffusion appeared to be Fickian. This has also been noted by Hori and colleagues,¹⁷ who observed Fickian dye diffusion when dyeing PET fibers with 1,4-diaminoanthraquinone in the presence of 1,1,2,2-tetrachloroethylene, *n*-butanol, and a mix of the two at 70°C for 5, 15, and 30 h.

The increase in the diffusion coefficient and the depth of diffusion of the dye, when compared with the sample dyed without carrier, illustrates the large effect of the carrier presence. This effect can also be seen in the increase in the K/S values for the dyed PET fabrics when compared with the control [Fig. 4(a)]. The increased depth of diffusion with the addition of carrier has been explained by Salvin¹⁸ as being due to the carrier displacing dye molecules near the surface of the substrate, allowing for dye diffusion away from the surface into the bulk. However, our data show that this is not the case with a bromobenzene and Disperse Orange 5 system. We found that the dye diffused into the film at a depth

Table III Results for Dye and Bromobenzene Diffusion in PET Film at 65°C when Applied Simultaneously from an Aqueous Bath

Exposure Time	Front Depth (nm)	Total Diffusion Depth (nm)	Front Velocity (nm/s) $r^2 = 0.963$	Diffusion Coefficient ($10^{-11} \text{ cm}^2/\text{s}$)	Concentration (10^{-3} g/cm^3)	
					RBS	NAA
Dye						
2 s		887 (327)		16 (10)	3.3 (4)	
5 s		557 (81)		6.7 (2)	0.9 (0.6)	9.2 (7)
10 s		613 (91)		1.7 (0.6)	2.6 (2)	9.3 (5)
Bromobenzene						
2 s	407 (45)	1340 (121)	6.10	1.3 (0.3)	1.3 (0.5)	
5 s	607 (81)	1323 (176)	6.10	1.5 (0.1)	1.8 (0.1)	1.8 (1)
10 s	687 (40)	1637 (11)	6.10	2.6 (0.7)	2.5 (0.2)	3.5 (2)
1 min						6.8 (2)
10 min						16 (2)
30 min						20 (5)
60 min						14 (0.7)

Average (standard deviation).

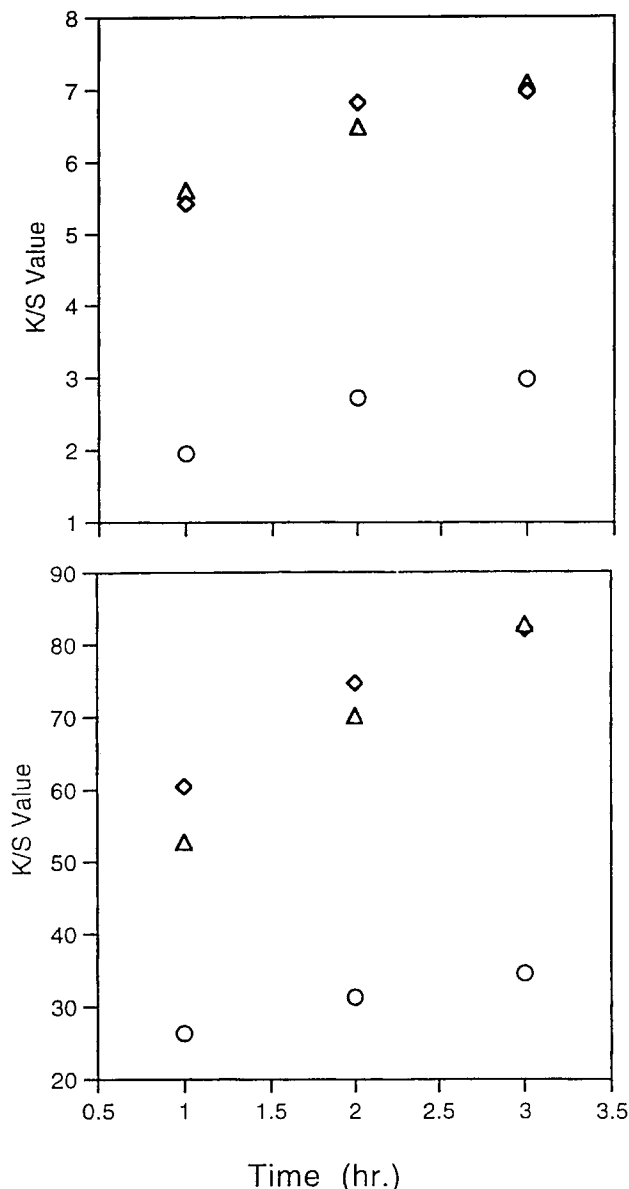


Figure 4 K/S values of polyester fabrics after dyeing with and without carrier: (a) 65°C (standard deviations were in the range of 0.04–0.16); (b) 90°C (standard deviations were in the range of 0.10–1.48). (\diamond) bromobenzene; (Δ) chlorobenzene; (\circ) control (no solvent).

equal to the front depth of the carrier. This is an indication that the dye is diffusing into the area near the surface of the film which has been swollen by the solvent.

Bromobenzene Diffusion at 65°C versus 90°C

In comparing the diffusion parameters of bromobenzene at the two temperatures, the most prominent difference is the change in the diffusion profile [Figs. 1(a) and 5(a)]. Below T_g the diffusion profile

of bromobenzene was found to be characteristic of case II diffusion, while above T_g the diffusion was Fickian.

The solvent concentration at the two temperatures was also found to differ for specimens treated for 10 min or longer. The uptake above T_g was lower than below T_g both when dye was present in the bath (Tables III and V) and when the carrier was applied independently of the dye (Tables I and IV). The increase in temperature increased the diffusion coefficient of the solvent, but no change was observed in the total diffusion depth with treatment times investigated.

The major effect of temperature, the change in diffusion profile from case II diffusion to Fickian diffusion, can be explained on the basis of the extent of thermal motion of the PET molecules at each temperature. Below T_g there is little motion of the polymer chains, and the diffusion of the solvent is restricted to the voids present in the polymer structure. The solvent must overcome the internal forces of the polymer which resist swelling before significant diffusion can occur. Thus, one observes case II diffusion. Above T_g the polymer molecules have significant molecular motion, reducing the barrier to the solvent diffusion. Thus the solvent diffuses in a Fickian manner. This change in diffusion profile from case II to Fickian with an increase in temperature has also been observed by Thomas and Windle¹⁴ when studying the diffusion of methanol into poly(methyl methacrylate).

The seeming anomaly in the NAA data, i.e., that the bromobenzene uptake decreases with temperature both in the presence and absence of dye (Tables I and IV, and Tables III and V, respectively), is likely due to the vapor pressure of the solvent at the two temperatures (Table VI). At 90°C, the bromobenzene has a vapor pressure of 100 mm, while at 65°C the vapor pressure is 40 mm.¹⁹ The increase in vapor pressure at the higher temperature results in an increase in the solvent activity in the vapor, or a decrease in the osmotic pressure, the driving force for diffusion of the solvent from the bath to the PET film. Therefore, at the higher temperature, less bromobenzene diffuses into the film.

Roberts and Solanki²⁰ noted that the diffusion coefficient of carrier increases as the concentration of the carrier in the PET increases. Since our exposure times were short and the resulting concentrations were low, we did not observe this effect at either 65°C or 90°C. One would expect from our results that the lower solvent concentration in the PET film at 90°C when compared to 65°C would result in smaller diffusion coefficients at the higher temperature. This is not the case; however, because

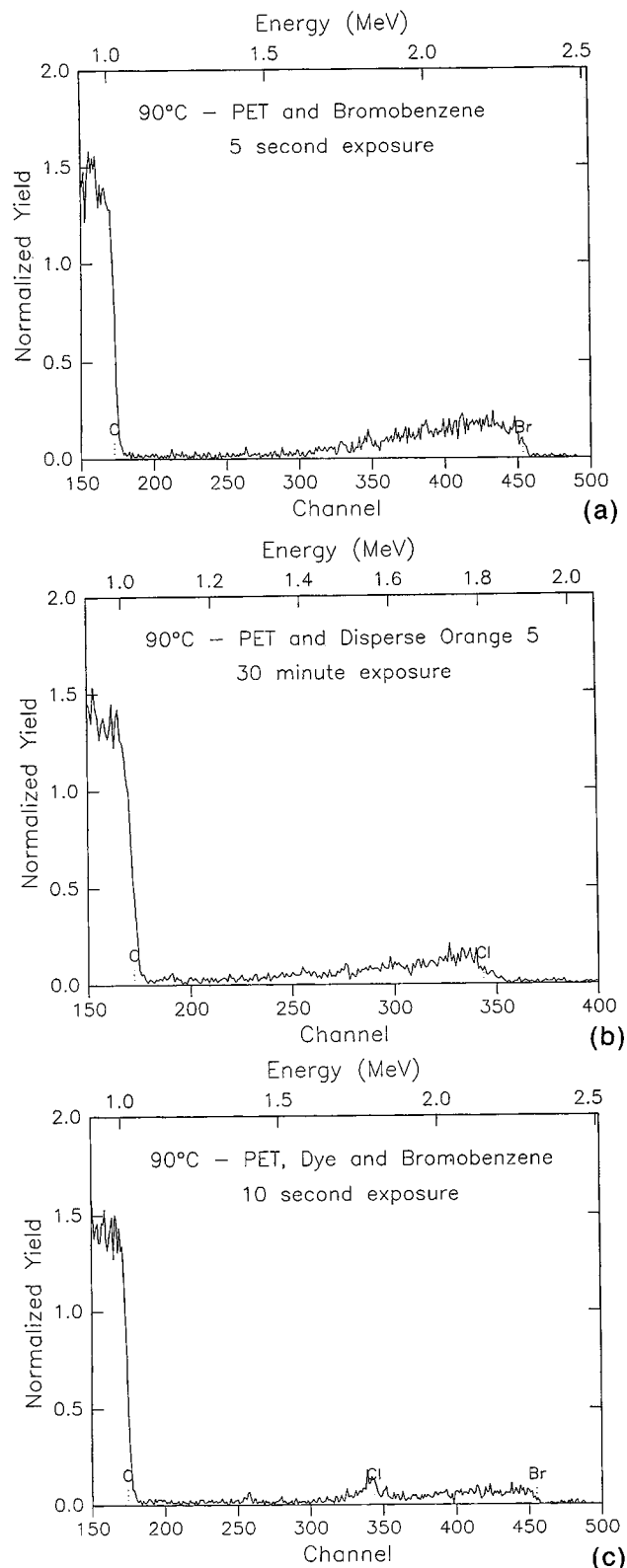


Figure 5 Typical RBS spectra at 90°C for (a) bromobenzene diffusion in PET film after 5 s exposure, (b) dye diffusion in PET film after 30 min exposure, and (c) dye and solvent applied simultaneously to PET film after 10 s exposure.

the higher temperature allows for more free volume in the polymer structure, diffusion takes place at a faster rate than at the lower temperature. A limiting factor in our research is the large variability in the results obtained using the higher temperature (90°C) and short exposure times. Thus, more replication would have been advantageous to more accurately determine the solvent concentration at each exposure time.

Dye Diffusion at 65°C Versus 90°C

In the NAA data, higher average dye concentration in the film was found at 90°C than at 65°C when the dye was applied alone (Table II). The dye was also found to have diffused much farther into the film and much faster at the higher temperature (Table VII), the diffusion coefficient increasing from 10^{-14} to 10^{-12} cm²/s and the diffusion depth from 400 to 1983 nm. RBS results showed the diffusion of the dye to be Fickian at 90°C [Fig. 5(b)] similar to results observed at 65°C (below T_g). Thus, temperature was found to have no effect on the diffusion mechanism of the dye, but the increase in temperature increased the depth of shade at each dyeing time for both the samples dyed with and without carrier [Fig. 4(a) vs. Fig. 4(b); note scale differences on y-axis]. The fact that dye diffusion at both temperatures was found to be Fickian is in agreement with the findings of Hori, Sato, and Shimizu,¹⁷ who investigated the diffusion of an anthraquinone dye into PET fibers in the presence of several dye carriers.

Simultaneous Diffusion at 65°C Versus 90°C

At both temperatures, the dye concentration increased significantly in the presence of bromobenzene (Table II). We found the diffusion coefficient of Disperse Orange 5 in PET film at 90°C to be on the order of 10^{-12} cm²/s without carrier (Table VII) and 10^{-10} cm²/s with carrier (Table V). These are similar to values reported by Olson and Mendoza-Vergara.²¹ These data support the hypothesis that the bromobenzene is plasticizing the PET, decreasing the viscosity of the polymer chains, and thus lowering the barrier to dye diffusion.

Above T_g of the PET film, it was found that both dye and the solvent exhibited Fickian diffusion profiles. The profile of neither species was affected by the introduction of the other species into the aqueous dyebath. The bromobenzene exhibited no significant differences in diffusion depth, diffusion coefficient, or concentration with increasing exposure time when applied alone or when applied in combination with the dye (Tables IV and V). Davis and Taylor²² reported that if a diffusant interacts with a substrate

Table IV Results for Bromobenzene Diffusion in PET Film at 90°C

Exposure Time	Total Diffusion Depth (nm)	Diffusion Coefficient (10^{-11} cm ² /s)	Solvent Concentration (10^{-3} g/cm ³)	
			RBS	NAA
5 s	2410 (780)	300 (200)	2.4 (2)	0.39 (0.1)
10 s	2575 (608)	260 (200)	2.9 (3)	0.70 (0.4)
15 s	2860 (358)	280 (200)	2.4 (2)	1.5 (1)
1 min				1.1 (0.3)
10 min				1.9 (0.5)
30 min				1.4 (0.2)
60 min				1.2 (0.2)

Average (standard deviation).

the diffusion coefficient will not be constant but will vary with concentration or time. We did not observe this effect, i.e., the diffusion coefficient remained constant over the short time exposure observed. However, from the results of Needles and Walker,¹⁶ we know that bromobenzene is a mild swelling agent for PET.

At both temperatures, the depth of shade of the dyed fabric obtained when the carrier was present was found to increase with an increase in the time of dyeing (Fig. 4), and when carrier was present the depth of shade obtained at equivalent dyeing times was greater. When dye and carrier are applied simultaneously the K/S data show that, although

the concentration of bromobenzene in the PET film at 90°C is lower than at 65°C, the depth of shade attained by the fabric increases greatly for equivalent time exposures [Fig. 4(a) vs. 4(b)]. Roberts and Solanki⁴ have concluded that carriers are less effective at higher temperatures by noting that the activation energy for diffusion of dyes into polymers at higher temperatures is lower, and thus carriers cannot affect the rates of diffusion of the dyes as greatly. From our NAA results (Table II), we find that the carrier does have more effect on the dye uptake at 65°C than at 90°C. Thus the increased depth of shade obtained at 90°C, which is a result of the increased dye uptake at that temperature, is

Table V Results for Dye and Bromobenzene Diffusion in PET Film at 90°C when Applied Simultaneously from an Aqueous Bath

Exposure Time	Total Diffusion Depth (nm)	Diffusion Coefficient (10^{-11} cm ² /s)	Concentration (10^{-3} g/cm ³)	
			RBS	NAA
Dye				
5 s	460 (1)	18 (1)	0.93 (0.2)	1.7 (1)
10 s	693 (104)	28 (4)	0.93 (0.3)	1.5 (1)
15 s				1.1 (0.3)
1 min				1.8 (0.7)
10 min				3.4 (1)
30 min				4.4 (1)
60 min				5.6 (1)
Bromobenzene				
5 s	1837 (1051)	310 (430)	5.0 (4)	0.24 (0.1)
10 s	2917 (671)	220 (190)	6.7 (6)	0.40 (0.3)
15 s				0.33 (0.1)
1 min				0.45 (0.1)
10 min				0.74 (0.3)
30 min				0.96 (0.1)
60 min				1.0 (0.1)

Average (standard deviation).

Table VI Vapor Pressures of Select Organic Solvents¹⁹

Vapor Pressure (mm)	Temperature (°C)	
	Bromobenzene	Chlorobenzene
40	68.6	49.6
100	90.8	70.7
400	132.3	110.0
760	156.2	132.2

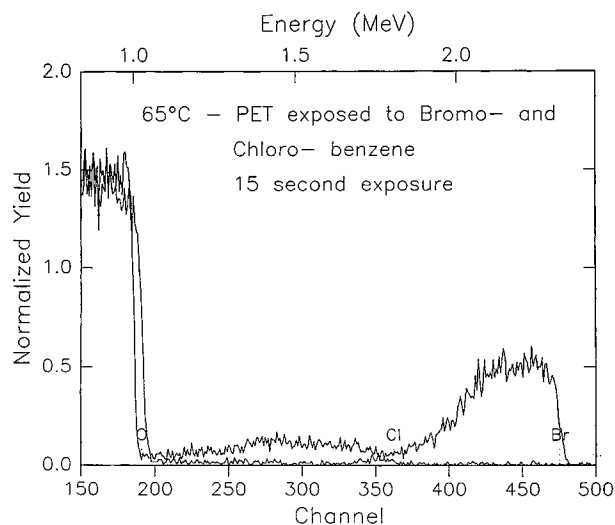
due to the increase in temperature coupled with the presence of carrier. It is possible that the carrier is also causing some swelling of the PET at the higher temperature but that the thermal motion of the polymer chains, which decreases the internal stresses within the structure, prevents the sharp front between the swollen and unswollen regions of the polymer that was seen at 65°C from being observed with the RBS at 90°C.

Solvent Effects

Although it is well known that the addition of certain organic solvents to an aqueous dyebath can increase the rate of dye uptake significantly, the selection of solvents for use as dye carriers is largely one of trial and error. We investigated the diffusion of bromobenzene and chlorobenzene both above and below the T_g of PET to determine how any differences in their diffusion mechanisms might affect their performance as dye carriers.

Below T_g for the PET film (65°C), the diffusion profiles for each of the solvents obtained from RBS were case II in character (Fig. 6). In comparing the chlorobenzene with the bromobenzene results for treatment times up to 1 min, the differences in the amount of solvent present in the PET for equivalent time exposures were not statistically different (Table VIII). However, for longer exposure times, the uptake of chlorobenzene is significantly lower than the uptake of bromobenzene. For both solvents, the diffusion coefficient and diffusion depth were found to increase with treatment time, and the front depth was found to be higher at the 10- and 15-s exposure times when the chlorobenzene results were compared to those of the bromobenzene (Table IX). No statistically significant differences were noted in the total diffusion depths.

In terms of the depth of shade, both solvents functioned as carriers, resulting in significantly darker shades. The depth of shade increased with increased dyeing time and temperature (Fig. 4). When comparing the bromobenzene and chloroben-

**Figure 6** Typical RBS spectrum for bromo- and chlorobenzene diffusion into PET film at 65°C after 15 s exposure.

zene results at 65°C, no depth of shade differences at the 1-h and 3-h dyeing times were observed, but after 2 h the bromobenzene-dyed fabric had a greater depth of shade than did the chlorobenzene-dyed fabric.

The chlorobenzene uptake of the PET at 90°C was too low to be measured accurately using RBS; thus NAA and color measurements were used to determine any differences in the carrier ability of the two solvents. Comparing the NAA results for the two solvents we found that, for equivalent time exposures, the only significant differences were that the bromobenzene uptake was higher after 15 s and 10 min than the chlorobenzene uptake (Table VIII). Depth of shade measurements at 90°C show that the depth of shade increases with time for both solvents [Fig. 4(b)]. Again, the 3-h dyeing resulted in the same depth of shade for the two solvents. When dyed for 1 and 2 h, a lower depth of shade was observed for chlorobenzene than for bromobenzene.

Table VII RBS Results for Dye Diffusion in PET Film at 90°C

Exposure Time	Total Diffusion Depth (nm)	Diffusion Coefficient (10^{-11} cm ² /s)	Dye Concentration (10^{-3} g/cm ³)
5 min	1300 (608)	0.5 (0.2)	3.1 (2)
10 min	1367 (551)	0.5 (0.4)	2.7 (0.6)
30 min	1983 (29)	0.3 (0.1)	4.9 (2)

Average (standard deviation).

Table VIII Solvent Uptake in PET Film as Determined by Neutron Activation Analysis

Exposure Time	Solvent Concentration (10^{-3} g/cm ³)			
	Bromobenzene		Chlorobenzene	
	65°C	90°C	65°C	90°C
5 s	1.0 (0.4)	0.39 (0.13)	0.46 (0.14)	0.21 (0.07)
10 s	2.0 (1.1)	0.70 (0.42)	0.80 (0.12)	0.22 (0.03)
15 s	2.9 (2.1)	1.5 (1.1)	0.92 (0.29)	0.24 (0.07)
1 min	5.3 (3.7)	1.1 (0.31)	1.4 (0.84)	0.36 (0.08)
10 min	12 (8.0)	1.9 (0.54)	2.4 (1.2)	0.69 (0.05)
30 min	18 (2.3)	1.4 (0.17)	2.2 (0.92)	0.88 (0.10)
60 min	13 (3.5)	1.2 (0.18)	2.3 (0.87)	0.92 (0.12)

Average (standard deviation).

The fact that both of the solvents exhibit case II diffusion characteristics below T_g of PET indicates that each solvent is interacting with the substrate and causing swelling at the near surface region (Fig. 6). This increase in volume allows more space in the structure into which the dye can diffuse, resulting in increased rates of dyeing and greater depth of shade than would be achieved were no solvent present.

The seeming anomalies in the data, i.e., that the bromobenzene uptake decreases with temperature and that the chlorobenzene uptake is less than that of the bromobenzene for longer exposure times at 65°C (Table VIII), are likely due to the vapor pressures of the solvents at the different temperatures (Table VI). At 90°C the bromobenzene has a vapor pressure of 100 mm, whereas the chlorobenzene has a vapor pressure of \sim 400 mm. At 65°C the vapor pressures are 40 mm and \sim 100 mm, respectively. As explained previously, while the vapor pressure increases, the osmotic pressure—the driving force for diffusion of the solvent into the PET film—decreases. Comparing the vapor pressures of the two solvents, it is seen that at a given temperature the vapor pressure of the chlorobenzene is higher than that of the bromobenzene, resulting in a lower osmotic pressure and thus a lower uptake of the chlorobenzene by the film.

Brown and Peters²³ report that bromine compounds are more effective than chlorine compounds in terms of carrier effectiveness. This is not evident in the depth of shade data in Figure 4. Carrier effectiveness has been explained using molecular interaction theory, a measure of molecular interaction being the solubility parameter. Two compounds with similar solubility parameters will be more likely to

interact than two compounds with widely differing solubility parameters. Plasticization is said to be due to the dispersion forces, but association forces are not to be disregarded when working with aqueous systems.⁵

The solubility parameters of bromobenzene and chlorobenzene are shown in Table X. It can be seen that the dispersion parameter is closer for the chlorobenzene and the PET than for the bromobenzene and the PET. However, since the treatments are taking place in aqueous solution, the association parameter must also be considered. In this case, the bromobenzene is more similar to the PET than the chlorobenzene. It is likely that the solubility differences cancel out, leaving us with two solvents which behave similarly in terms of carrier effect. This is illustrated by the similarity of the bromobenzene and chlorobenzene K/S results [Fig. 4(a,b)].

This study found that both bromo- and chlorobenzene increase the amount of dye uptake of polyester. Both solvents appear to function as dye carriers by similar mechanisms, as might be expected. Below T_g of the PET film both solvents exhibited case II diffusion. This indicates that the solvents are swelling the near surface regions of the film and creating more void volume into which the dye can diffuse. The effect of this additional volume is illustrated by the significant increases in the K/S values of polyester fabrics dyed in the presence of the solvents. Above T_g of the PET film, the effects of both solvents were coupled with the increase in temperature to further decrease the viscosity of the polymer chains, allowing for increased dye uptake when compared with the dye uptake when no solvent was present. Factors which may be important to consider when choosing a solvent as a dye carrier are the

Table IX RBS Results for Bromo- and Chlorobenzene Diffusion in PET Film at 65°C

Exposure Time	Front Depth (nm)	Total Diffusion		Diffusion Coefficient (10^{-11} cm ² /s)	Solvent Concentration (10^{-3} g/cm ³)
		Depth (nm)	Front Velocity (nm/s)		
Bromobenzene					
5 s	482 (39.6)	1308 (94.3)	23.2	6.0 (0.86)	1.5 (0.28)
10 s	483 (28.9)	1483 (28.9)	23.2	11.3 (0.85)	2.4 (0.18)
15 s	625 (119)	2150 (617)	23.2	13.5 (5.4)	2.5 (1.1)
Chlorobenzene					
5 s	600 (10)	1300 (141)	37.5	11.2 (5.3)	1.3 (0.24)
10 s	725 (35.4)	1775 (106)	37.5	20.6 (2.6)	1.6 (0.56)
15 s	975 (106)	1925 (106)	37.5	26.2 (0)	1.9 (0.53)

Average (standard deviation).

vapor pressure of the solvent at the required dyeing temperature and the solubility parameter of the solvent.

CONCLUSION

One of the major goals of this study was to quantify the RBS technique in order to determine the diffusion parameters of a dye and a solvent in PET film. We found that RBS concentration results correlated well with the concentration results obtained using neutron activation analysis, a sensitive technique for obtaining a bulk elemental analysis of samples. Therefore, we concluded that RBS is an extremely useful technique for obtaining accurate diffusion information of species when applied independently and simultaneously.

RBS allowed for the determination of the mechanism by which bromobenzene and chlorobenzene functioned as dye carriers. The case II diffusion profiles obtained for the diffusion of these solvents below T_g (65°C) of the PET film revealed that swelling of the substrate was occurring at the near-surface regions, allowing for more void space into which the dye could diffuse. We found that the diffusion depth of the dye was equivalent to the thickness of the swollen polymer region (~ 600 nm) and that the

presence of the solvent increased the diffusion coefficient of the dye from 10^{-14} to 10^{-11} cm²/s.

Above T_g (90°C), the solvent diffusion was Fickian. However, the enhancement of the dye uptake, even in the presence of increased thermal motion of the polymer molecules at the higher temperature, indicates that the solvent continues to swell the polymer to some extent. That the diffusion profile above T_g does not indicate the sharp front observed in Case II diffusion results from the decrease in polymer viscosity, due to thermal motion, behind the swollen region. Thus no or little resistance to solvent diffusion is encountered. At 90°C, the diffusion coefficient of the dye increased from 10^{-12} to 10^{-10} cm²/s in the presence of the solvent.

The diffusion parameters of bromobenzene and chlorobenzene in PET film were compared. Both solvents showed similar diffusion mechanisms, exhibiting case II diffusion below T_g and Fickian diffusion above T_g . We noted that the vapor pressure and the solubility parameters of the solvents have an effect on the amount of solvent taken up by the film. In this study, the solvents were found to be equally effective as carriers for Disperse Orange 5.

The dye was found to diffuse in a Fickian manner both above and below T_g of the PET film. The presence of the solvent in the dyebath at each temperature had no effect on the diffusion mechanism of the dye. Neither did the presence of the dye in the dyebath have an effect on the diffusion parameters of the solvent at either temperature. Thus we concluded that there was no competition between the two species for dyeing sites within the polymer.

Table X Solubility Parameters of Select Species (MPa^{1/2})¹⁹

Solvent	δ_D	δ_A	δ_H	δ_T
Bromobenzene	20.5	5.5	4.1	21.7
Chlorobenzene	19.0	4.3	2.0	19.6
PET	19.1	8.7	6.0	22.1
Water	15.6	16.0	42.3	47.8

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