

The permeability of a disazothiophene dye solute in polymer matrices above the glass transition

A. T. Slark* and J. E. Fox†

*ICI Imagedata, Brantham, Manningtree, Essex CO11 1NL, UK
 (Revised 16 August 1996)*

The permeability of a functionalized dye solute in various amorphous polymers above the glass transition temperature has been investigated using dye diffusion thermal transfer printing. A disazothiophene dye molecule was transferred from a constant dye-donor polymer matrix to a variety of dye-acceptor polymer matrices. All dye-acceptor polymers were amorphous, but their chemical structures, glass transition temperatures and solubility behaviours were modified. Dye transfer during a constant print cycle time (i.e. a constant temperature profile) was found to depend on both the diffusivity and the solubility of the solute. Using the solution-diffusion model of permeability as a starting point, equations were developed relating solute permeability to structural characteristics of the components. An excellent correlation has been made for solute permeability as a function of polymer T_g and dye-polymer affinity as defined by solubility parameter differences. © 1997 Elsevier Science Ltd.

(Keywords: permeability; solute; glass transition)

INTRODUCTION

There have been many studies on the permeability and diffusion of solutes in polymer matrices. Generally, distinctions have been made between small molecules (gases) and large molecules (liquids and vapours) which interact strongly with the polymer¹. For diffusivity, it is generally accepted that for translational motion of a solute to occur, there must be a space of sufficient size for the molecule to move into. It has been established that diffusivity will partly depend on the size of the solute, and it is possible that diffusion rates can be coupled to relaxational processes in polymers². Small molecules will readily permeate through glassy polymers if they are soluble. Molecules comparable with or larger in size than the polymer repeating unit require a co-operative movement of several polymer segments to take place. Therefore, large molecules with dimensions similar to or greater than the repeating unit of a polymer matrix will require the large space created by the chain co-operative movements characteristic of T_g ³. Such large molecules are known to exhibit a step change in the diffusion coefficient at T_g . Generally, a distinction is made between transport properties below T_g in glassy polymers and diffusion above T_g in rubbery polymers with the former being more complicated⁴. Glasses have long relaxation times, consist of a non-homogeneous environment and have been described by dual mode sorption. However, rubbers have short relaxation times where equilibrium is established quickly. This paper reports the transport properties of a

large dye solute with a molecular weight of 466 g mol^{-1} in various amorphous polymers above T_g .

The control of dye transport is an important phenomenon in the dyeing of polymer fibres for coloured fabrics and the dyeing of polymer films for imaging applications. There are several publications in the literature where the importance of the polymer glass transition temperature to dye transport is highlighted in the conventional dyeing of fibres^{5,6} and films^{7–9}. It is known that there is a step change in the uptake of dyes at the glass transition temperature of the polymer¹⁰. This can be explained by the fact that the molecular weight of the dye is at least similar in size to the polymer repeating unit, and this results in a step change in diffusion coefficient at T_g . The control of dye delivery is also important in dye diffusion thermal transfer printing, which is a method for producing high-quality continuous tone colour images from an electronic source¹¹. The printing process involves the transfer of dye from a donor ribbon to an acceptor sheet, which are brought into intimate contact at high temperature and pressure. The quantity of dye transferred depends on the temperature reached during printing. The temperature of dye transfer and the print time can vary, but maximum values are typically 300°C and 12 ms, respectively. Images are produced by the sequential transfer of dye from yellow, magenta and cyan panels which are repeated in series along the length of the ribbon. Different colours are produced by controlling the relative amounts of yellow, magenta and cyan dye at each pixel. In addition to being technologically important, a thermal transfer printer represents a well-controlled and defined experimental test-bed for studying the diffusion of solutes in polymers. Additionally, the fact that the solutes are dyes which absorb light in the

* To whom correspondence should be addressed. Current address: ICI Acrylics, PO Box 90, Wilton, Middlesbrough, Cleveland TS90 8JE, UK
 † Current address: Domino UK Limited, Bar Hill, Cambridge CB3 8TU, UK

visible part of the spectrum means that it is easy to detect their movement.

Typically, both the donor ribbon and acceptor sheet for thermal transfer printing are multilayer structures, with each layer performing a particular function¹¹. The dye transfers from a polymer coating in the donor sheet (dye-donor) to an acceptor polymer coating in the receiver sheet (dye-acceptor). It has been shown that the mechanism for dye transfer is diffusion between polymers rather than sublimation¹². Therefore, the dye transfer process can be viewed as permeability from a dye-donor polymer to a dye-acceptor polymer where the temperature of transport is above the glass transition temperatures of both the donor and acceptor matrices. The dye transfer process has been modelled previously. Hann and Beck¹¹ illustrated that the use of a model involving diffusion coefficients and partition coefficients was reasonable in predicting the dye transfer. More recently, Shinozaki and Hirano¹³ have proposed a mechanism involving adsorption followed by diffusion.

In previous work¹⁴, it has been shown that dye diffusion coefficients determined by Rutherford backscattering correlate well with a free volume interpretation of diffusion. It has also been demonstrated¹⁵ that dye delivery from various dye-donor matrices to a constant dye-acceptor is controlled by the free volume in, and the glass transition of, the dye-polymer blend in the donor matrix. The latter is strongly influenced by the interactions between the dye and the dye-donor polymer¹⁶. The work presented here describes the converse situation where the influence of the dye acceptor matrix on the transport characteristics of a coloured solute with a molecular weight of 466 g mol^{-1} is investigated using a constant dye-donor matrix.

METHOD

Materials

The dye used in this study (illustrated in *Figure 1*) was a disazothiophene molecule with a molecular weight of 466 g mol^{-1} and a melting point of 210°C supplied by Zeneca Specialties. *Poly(vinyl butyral)* (PVB; BX-1, obtained from Sekisui Chemicals) was used as the dye-donor matrix, containing 65% butyral, 33% vinyl alcohol and 2% vinyl acetate.

Various polymers were used as dye-acceptor matrices. *Polystyrene* was used as supplied by BDH Chemicals. PVB; BX-1 was used as previously defined. *Poly(α -methyl styrene)* was used as supplied by the Aldrich Chemical

Company. *Poly(methyl methacrylate)* was used as supplied by Zeneca Resins as Neocryl B723. *Type A polyesters* were synthesized by the copolymerization of terephthalic acid (TA), isophthalic acid (IPA), azaleic acid (AZA), neopentyl glycol (NPG) and ethylene glycol (EG). *Type B polyesters* were synthesized by the copolymerization of IPA, naphthalene dicarboxylic acid (NDA), AZA, NPG and EG. *Type C polyesters* were synthesized by the copolymerization of IPA, sulfobisbenzoic acid (SBBA), AZA, NPG and EG. The structures of the polyesters are displayed in *Table 1*. All polyesters were used as supplied by the ICI Wilton Centre.

T_g measurements

A Perkin-Elmer DSC-4 instrument was used to characterize the glass transitions of the polymers used as dye-acceptor layers. An indium standard was used for calibration, and a heating rate of $20^\circ\text{C min}^{-1}$ was employed. Samples were heated to high temperature and rapidly cooled to give the samples the same thermal history, followed by determination of T_g during the second run. For the determination of the T_g of the dye-polymer donor film, measurements were made during the first run. The dye-donor polymer mixture was applied with a thickness of approximately $3 \mu\text{m}$ from tetrahydrofuran (THF) onto bare polyester $3.5 \mu\text{m}$ base and dried for 30 s at 110°C . An identical area of polyester base without coating and which received the same thermal treatment was used as a reference. The software subtracted the reference from the sample, providing the T_g of the dye-polymer coating.

Dye-polymer blend donor films

The dye was mixed with PVB (1/2 w/w) and dissolved in THF solvent. Donor films were created by coating this dye-polymer mixture onto a thin $6 \mu\text{m}$ poly(ethylene terephthalate) (PET) base film which contained a

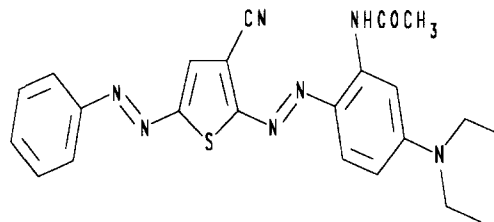


Figure 1 The structure of the disazothiophene dye solute

Table 1 Structures of polyesters used as dye-acceptor layers (values are % (w/w))

Type	Number	TA	IPA	NDC	SBBA	AZA	NPG	EG
A	1	29.5	29.5	—	—	—	35.5	5.5
A	2	27.4	28.3	—	—	3.2	35.3	5.8
B	3	—	20.2	43.5	—	—	31.1	5.2
B	4	—	13.5	42.5	—	8.0	30.0	6.0
B	5	—	12.7	41.8	—	10.0	29.0	6.5
B	6	—	6.0	43.0	—	16.0	28.3	6.7
C	7	—	20.7	—	48.2	—	26.9	4.2
C	8	—	10.5	—	48.8	11.3	23.5	5.9
C	9	—	9.0	—	48.5	12.6	24.8	5.1
C	10	—	4.5	—	48.3	18.3	21.9	7.0

thermally resistant backcoat on the rear side. The dye-polymer mixture was coated using a gravure coating technique with air impingement drying at 110°C. The transformation from dilute solution to solid solution is rapid (<1 s), yielding a supersaturated solution of dye in polymer. This treatment was shown to be effective in removing THF to low levels without causing the dye to phase separate. D.s.c. on the dye-polymer coating was found to give a single glass transition temperature of 45°C. The dye-polymer layer was supercoated with a thin 0.05 μm layer of poly(hydroxypropylmethylcellulose) (Methocel E50, obtained from the Dow Chemical Company) from a methanol/water solution. This layer was required to prevent adhesion between the dyecoat and receiver layers under the elevated temperature and pressure during the thermal transfer printing process.

Dye-acceptor films

Acceptor sheets were created by coating 4 μm layers of the dye-acceptor polymers previously defined onto PET base ('Melinex 990', obtained from ICI Films) with a thickness of 125 μm. The polymers were dissolved in THF solvent and coated onto the PET base using a wire bar. The coatings were dried by placing the receiver sheet in an oven at 140°C for 3 min. D.s.c. on films coated and dried in a similar fashion, but onto thin 3.5 μm PET base, showed that these films had similar T_g values to the solid polymer samples. This indicated that residual solvent had been removed effectively.

Thermal transfer printing

The donor sheet and receiver sheet were then placed with the dye-donor and dye-acceptor layers in intimate contact. The transport of dye was initiated using a thermal transfer printer. After printing, the donor sheet and receiver sheet were separated and the amount of dye which had transferred to the acceptor layers was determined by using a Macbeth TR1224 optical densitometer. An average of five measurements was made at each print time.

RESULTS AND DISCUSSION

Effects of acceptor polymer structure

Table 2 shows the glass transition temperatures and solubility parameters of all polymers used as acceptor layers, in addition to optical density measurements (OD) at constant print times of 13, 11 and 9 ms. Solubility parameters (δ_p) were calculated according to the group contribution method of Fedors¹⁷ by choosing the appropriate average repeating unit of the polymer structures, where

$$\delta_p = \left(\frac{E}{V} \right)^{1/2} \quad (1)$$

E is the sum of the cohesive energy of the functional groups per average repeating unit and V is the sum of the molar volume of the functional groups per average repeating unit. The calculations were based on the tabulated group contributions reproduced by Van Krevelen¹⁸. There are seven different types of dye-acceptor polymer with a range of T_g (49.3–110.7°C) and δ_p (20–27 (J cm⁻³)^{1/2}). For the polyester variants, NPG and EG were used as the diol throughout. For the diacid component, the main constituent varies from TA to NDA to SBBA for types A, B and C, respectively. The polymers have varying amounts of AZA to act as a plasticizing comonomer in order to control T_g , and this is very effective, which is evident from a comparison of the series B3–B6 and the series C7–C10 in Table 1. Within these series, the incremental decrease in T_g is accompanied by a slight decrease in the solubility parameter of the polymer resulting from the enhanced aliphatic character (due to the incorporation of AZA). The data in Table 2 show that both the T_g and solubility characteristic of the acceptor polymer have a significant influence on dye transport from the constant donor matrix. It can be seen that for polymers with approximately constant solubility parameter (for example the comparison of polyesters B3–B6), the rate of dye transfer increases as T_g decreases. In addition to this, to a first approximation, the rate of dye transfer increases as the polymer solubility parameter increases for polymers with similar T_g (for example the

Table 2 Characterization of dye-acceptor polymers

Polymer type ^a	T_g (°C)	δ_p ((J cm ⁻³) ^{1/2}) ^b	OD (13 ms)	OD (11 ms)	OD (9 ms)
PS (polystyrene)	108.4	21.59	1.03	0.75	0.48
PAMS (poly(α -methylstyrene))	79.0	20.57	0.87	0.69	0.47
PVB (poly(vinylbutyral))	83.8	23.00	1.52	1.15	0.77
PMMA (poly(methyl methacrylate))	110.7	20.32	0.71	0.52	0.34
Polyester A1	59.3	24.81	1.68	1.13	0.67
Polyester A2	57.6	24.53	1.74	1.24	0.70
Polyester B3	88.2	25.98	1.48	1.01	0.61
Polyester B4	67.6	25.40	1.61	1.09	0.65
Polyester B5	62.8	25.31	1.67	1.12	0.66
Polyester B6	51.8	24.95	1.76	1.18	0.68
Polyester C7	94.7	26.86	1.27	0.91	0.58
Polyester C8	64.1	26.33	1.49	1.04	0.61
Polyester C9	58.0	26.18	1.54	1.07	0.63
Polyester C10	49.3	25.97	1.81	1.12	0.65

^a See Table 1 for details of polyester samples

^b The dye solubility parameter $\delta_d = 24.38$ (J cm⁻³)^{1/2}

comparison of PAMS, PVB and polyester B3). These observations suggest that dye transfer under the conditions imposed by thermal transfer printing is controlled partly by kinetic factors (the influence of T_g) and thermodynamic factors (the influence of solubility parameter).

Analytical model based on a solution-diffusion mechanism

The dye transfer process occurs at temperatures of 150–300°C at the interface of dye-donor and dye-acceptor, well above the glass transition temperatures of the dye-donor and dye-acceptor matrices. It should be noted that the temperature is not discrete during dye diffusion thermal transfer printing. During a particular print time, there is a temperature distribution since the temperature rises, peaks at a maximum and then falls¹¹. Therefore, the printing process provides a very well-defined, constant temperature profile or cycle rather than a fixed, single temperature. Previous mathematical modelling¹¹ indicates that the maximum temperature at the interface between the dye-donor and dye-acceptor polymer matrices is 300, 280 and 260°C for print times 13, 11 and 9 ms, respectively. From the solution-diffusion model of permeability¹⁹, the permeability coefficient (P) of a solute in a polymer can be expressed as

$$P = DS \quad (2)$$

where D is the diffusion coefficient of the solute in the polymer and S is the solubility coefficient. An expression for permeability was developed by expanding D and S in terms of the structural characteristics of the solute and the polymer.

Firstly, consider diffusivity. There are many cases where solute diffusion coefficients have been expressed by molecular models in an Arrhenius form with an associated activation energy. Numerous past works have discussed activation energies for the diffusion of large and small, polar and non-polar solutes through a number of polymers both below and above the glass transition temperature. These include the works of Barrer²⁰, Meares²¹, Brandt²² and DiBeneditto and Paul^{23,24}. More recently, further sophistication has been added by Pace and Datyner^{25,26}. In contrast to this, several authors have concluded that the temperature dependence of the diffusion coefficient is adequately described using a free volume interpretation. Contributions to the explanation of solute transport via a free volume mechanism include those of Bueche²⁷, Ferry²⁸, Fujita²⁹, and Cohen and Turnbull³⁰. More recently, Vrentas and Duda³¹ have proposed a free volume model which is particularly applicable to penetrants with high solubilities. The most recent extensions to free volume elucidations come from Mauritz and Storey^{32,33}, who have formulated a theory to describe the diffusion of large penetrants in amorphous polymers above T_g . Zhang and Wang^{34,35} used forced Rayleigh scattering (FRS) to show that the variation of dye diffusion coefficient above T_g is well represented by the Williams-Landel-Ferry (WLF) equation³⁶. Similar conclusions have been made by various authors on different systems using FRS. This includes Ehlich and Sillescu³⁷ on photo-reactive dyes in polystyrene, poly(ethyl styrene), poly(methyl methacrylate), poly(ethyl methacrylate) and polycarbonate; Xia *et al.*³⁸ on camphorquinone in poly(aryl ether ether ketone); and Kim *et al.*³⁹ on

cyclophane dye in polystyrene, poly(vinyl acetate) and poly(vinyl methyl ether). More recently, Byers⁴⁰ has shown that the diffusion of dyes in polycarbonates above T_g also obeys WLF-type relationships. It should be noted that in all of these previous studies, the dye concentration is low (<1%) in comparison to the work presented in this paper. In the work presented here, the dye concentration in the donor matrix is 33% (w/w). In related publications, we have also shown that dye diffusion during thermal transfer printing can be adequately described by free volume considerations^{14,15} when the dye concentration in the donor matrix is high (33–50% w/w).

Fujita²⁹ stated that the diffusion coefficient of a solute can be related to free volume by the equation

$$D = RTA_d \exp\left(\frac{-B_d}{f}\right) \quad (3)$$

where R is the gas constant, T is the temperature, f is the fractional free volume and both A_d and B_d are constants.

Now consider solubility. The solubility coefficient S can be described by the equation¹⁹

$$S = S_0 \exp\left(\frac{-\Delta H}{RT}\right) \quad (4)$$

where S_0 is the solubility coefficient as concentration tends to zero and ΔH is the heat of mixing between two components, which can be defined by the equation^{18,19}

$$\Delta H = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \quad (5)$$

where ϕ_1 and ϕ_2 are the volume fractions of solute and polymer, respectively, and δ_1 and δ_2 are the solubility parameters of the solute and polymer, respectively. For the permeability of a dye solute (ϕ_d, δ_d) in a polymer (ϕ_p, δ_p), equation (5) becomes

$$\Delta H = \phi_d \phi_p (\delta_d - \delta_p)^2 \quad (6)$$

Substituting for equation (6) into equation (4) gives

$$S = S_0 \exp\left(\frac{-[\phi_d \phi_p (\delta_d - \delta_p)^2]}{RT}\right) \quad (7)$$

From equation (2)

$$\ln P = \ln D + \ln S \quad (8)$$

Substituting equations (3) and (7) into equation (8) gives

$$\ln P = \left[\ln(RTA_d) - \left(\frac{B_d}{f}\right) \right] + \left[\ln S_0 - \left(\frac{\phi_d \phi_p (\delta_d - \delta_p)^2}{RT}\right) \right] \quad (9)$$

R is constant and T has a constant profile at a constant print time. The dye concentration in the dye-donor system is relatively high (and constant), and to a first approximation both ϕ_d and ϕ_p are independent of the dye-acceptor matrix. If it is further assumed that A_d , B_d and S_0 are invariant for solute-polymer combinations when the solute is constant, then equation (9) becomes

$$\ln P = a - b\left(\frac{1}{f}\right) - c(\delta_d - \delta_p)^2 \quad (10)$$

It is known that the free volume is constant up to T_g and increases linearly with temperature above T_g , the fractional free volume $f (= v_f/v)$, where v_f is the free

volume between molecules and v is the total volume) being given by

$$f = f_g + \alpha(T - T_g) \quad (11)$$

where f_g is the fractional free volume at the glass transition, and α is the difference between the expansion coefficients of the liquid (α_l) and the expansion coefficient of the glass (α_g), i.e. $\alpha = (\alpha_l - \alpha_g)$. In the WLF interpretation of free volume³⁶, both f_g and α are found to have universal values of 0.025 and 4.8×10^{-4} , respectively. Also, since the temperature profile during thermal transfer printing is fixed at constant print time, then f is proportional to $-T_g$, and equation (10) becomes

$$\ln P = a + b\left(\frac{1}{T_g}\right) - c(\delta_d - \delta_p)^2 \quad (12)$$

Comparison of experimental data and the analytical model

Regression analysis was performed on equation (12) for $\ln P$ as a function of $1/T_g$ and $(\delta_d - \delta_p)^2$ where:

- P is measured by the optical density of dye in the acceptor polymer after transfer;
- T_g is the measured T_g of the dye-acceptor polymer;
- $(\delta_d - \delta_p)$ is the solubility parameter difference between the dye and acceptor polymer calculated via the Fedors method.

The regression equation for the data at a print time of 13 ms (corresponding to a temperature profile of 150–300°C) is

$$\ln P = -0.449 + 336\left(\frac{1}{T_g}\right) - 0.0454(\delta_d - \delta_p)^2 \quad (13)$$

with a correlation coefficient $r = 0.99$. The data according to this equation are plotted in Figure 2. It can be seen from both the correlation coefficient and the appearance of Figure 2 that the correlation is excellent. This occurs despite possible experimental errors in formulation and coating in addition to potential variations in the rate of dye transfer and T_g measurement. Additionally, literature suggests that at best, the solubility parameters are correct to ± 0.8 (J cm⁻³)^{1/2}.⁴¹ The equation is relatively straightforward since it only contains four parameters which require two measurements (solute permeability and polymer T_g) and two calculations (the solubility parameters of both the solute and the polymer). For comparison, permeability was also correlated with T_g only, ignoring the effect of dye-polymer affinity. These

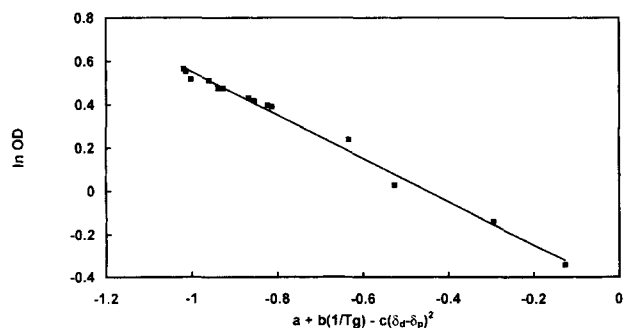


Figure 2 The permeability of a disazothiophene dye solute into various dye-acceptor polymers as a function of polymer T_g and dye-polymer solubility parameter difference, at a print time of 13 ms (maximum temperature $\sim 300^\circ\text{C}$). The correlation coefficient $r = 0.99$

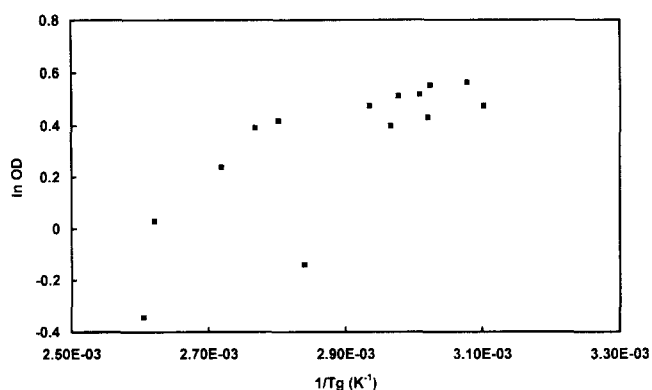


Figure 3 The permeability of a disazothiophene dye solute into various dye-acceptor polymers as a function of polymer T_g only, at a print time of 13 ms (maximum temperature $\sim 300^\circ\text{C}$)

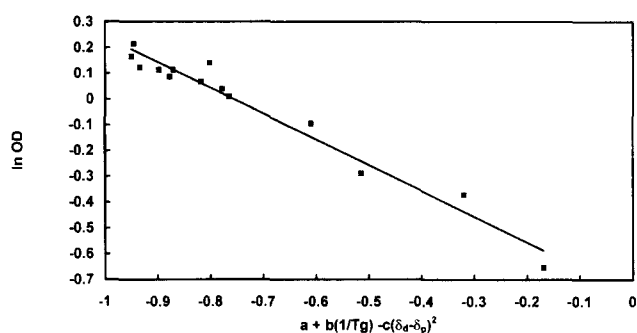


Figure 4 The permeability of a disazothiophene dye solute into various dye-acceptor polymers as a function of polymer T_g and dye-polymer solubility parameter difference, at a print time of 11 ms (maximum temperature $\sim 280^\circ\text{C}$). The correlation coefficient $r = 0.96$

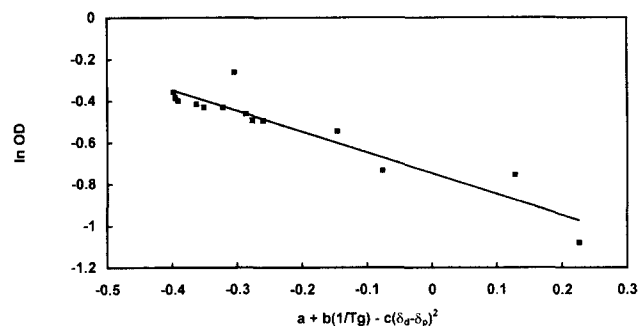


Figure 5 The permeability of a disazothiophene dye solute into various dye-acceptor polymers as a function of polymer T_g and dye-polymer solubility parameter difference, at a print time of 9 ms (maximum temperature $\sim 260^\circ\text{C}$). The correlation coefficient $r = 0.88$

Table 3 Regression analysis of equation (12) for different print times

Print time (ms)	T_{\max} ($^\circ\text{C}$) ^a	a ^b	b ^b	c ^b	r ^c
13	300	-0.449	336	0.0454	0.99
11	280	-0.756	313	0.0392	0.96
9	260	-0.746	132	0.0346	0.88

^a T_{\max} is the predicted maximum temperature

^b a , b and c are the coefficients in equation (12)

^c r is the correlation coefficient

data are illustrated in *Figure 3*, and demonstrate that, while permeability tends to decrease as T_g increases ($1/T_g$ decreases), there is substantial scatter in the data. Therefore, it is inappropriate to consider T_g alone since dye-polymer affinity has a substantial effect on the correlation.

Figures 4 and *5* illustrate the data plotted according to equation (12) for two further different print times (11 and 9 ms, respectively) corresponding to two different temperature regimes (predicted temperature ranges of 150–280 and 150–260°C, respectively). The coefficients a , b , c and the correlation coefficients for the regression analysis of the data represented in *Figures 2*, *4* and *5* are illustrated in *Table 3*. It can be seen that the description of permeability as a function of polymer glass transition and dye-polymer solubility parameter difference is appropriate for these different temperatures which are all well above the glass transitions of the dye-donor and dye-acceptor matrices. The results suggest that the transport of the dye from a constant donor matrix to various acceptor matrices above T_g is described adequately by a solution-diffusion mechanism. The closer the solubility parameters of the dye and acceptor polymers, the greater the affinity of the acceptor polymer for the dye; this results in higher dye solubility and higher dye transfer. The adequate prediction of dye-polymer affinity by solubility parameter match could be viewed as surprising. Some of the assumptions implicit in solubility parameter theory⁴² are:

- interaction forces act between molecule centres;
- mixing is random;
- the geometric mean assumption holds for separate contributions;
- strong polar and hydrogen bonding forces are non-directional.

Given that both the dye and several of the polymer structures involve possible strong polar and hydrogen bonding interactions, it seems likely that these assumptions will be violated and yet the use of solubility parameters is effective. One explanation for this is that specific interactions could be significantly reduced at higher temperatures making them insignificant. Attempts were made to correlate the data using separate component solubility parameters for dispersion, polar and hydrogen bonding forces from group contributions¹⁸. However, these correlations were inferior to those obtained using the overall total solubility parameters. It should be noted that in a separate publication¹⁶ we have successfully used δ_{ph} (the average of polar and hydrogen bonding solubility parameters) to describe the effect of dye-polymer affinity on the glass transition temperature of dye-polymer blends, where the temperatures were much lower than those experienced in this work. This suggests that the relative contribution of δ_{ph} could increase with decreasing temperature resulting in the increased experimental scatter as the maximum temperature decreases from 300 to 260°C.

The results agree with the analytical model, part of which assumes that diffusivity is controlled by the T_g of the acceptor polymer, independent of the type of polymer used with the interval $(T - T_g)$ likely to have significance. This suggests that the large-scale co-operative movement characteristic of T_g represents a large step-change in the diffusion coefficient of the solute molecule as a function

of temperature. This coupling of diffusion to the glass transition may not be surprising given that the molecular weight of the dye is 4–5 times that of a typical repeating polymer unit, as previously discussed. Additionally, the exclusive dependence of diffusivity on T_g implies that the diffusion coefficient of a particular solute at high temperatures well above T_g does not depend on the differences in interactions between the dye and the various dye-acceptor matrices. This may result from the high temperatures experienced by the dye and polymer matrices (150–300°C depending on the print time) by increasing free volume and reducing the effectiveness of intermolecular forces at high temperatures on diffusion coefficients. Recent work by Byers⁴⁰ on the diffusion of dyes in polycarbonate above T_g at 180°C agrees with this interpretation. Numerous dye structures were investigated, partly to explore the effects of intermolecular hydrogen bonding. He found that dye diffusion in this constant matrix at this temperature was controlled by the shape of the dye molecule with no discernible effect of intermolecular forces on diffusion coefficients.

CONCLUSIONS

The transport of solutes has been studied using dye diffusion thermal transfer printing. A dye was transferred from a constant dye-donor matrix to various dye-acceptor matrices well above the glass transition temperatures of the components. Under these conditions, dye transfer at a constant print time and for a constant temperature profile appears to be influenced by both kinetic and thermodynamic factors. Dye transfer was found to increase when the acceptor polymer T_g was lower and/or when the dye was more compatible with the dye-acceptor polymer, the latter being characterized by a closer solubility parameter match between the two components.

For a constant temperature profile, dye permeability is a function of both diffusivity and solubility. Using the solution-diffusion model of permeability as a starting point, equations were developed to correlate solute permeability with dye and polymer structural characteristics. An excellent correlation has been made for solute permeability as a function of dye-acceptor polymer T_g and the solubility parameter difference between dye and dye-acceptor polymer. It is thought that the limit of applicability is the transport of large solutes in amorphous polymers above T_g and in the absence of strong specific interactions.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the assistance of Alan Butters (ICI Imagedata) for his contribution and many useful discussions during the course of this work. We would also like to acknowledge the help of our ICI colleagues Dr Peter Mills, Dr Bill MacDonald and Kevin Payne (ICI Wilton Centre) for the polyester synthesis. The authors also wish to thank Dr Robert Glen (ICI Imagedata) for allowing publication of this work.

REFERENCES

1. Stannett, V., in *Diffusion in Polymers*, ed. J. Crank and G. S. Park. Academic Press, London, 1968, Ch. 2.

2. Kumins, C. A. and Kwei, T. K., in *Diffusion in Polymers*, ed. J. Crank and G. S. Park, Academic Press, London, 1968, Ch. 4.
3. Fujita, H. in *Diffusion in Polymers*, ed. J. Crank and G. S. Park. Academic Press, London, 1968, Ch. 3.
4. Stern, S. A. and Trohalaki, S., *ACS Symp. Ser.*, 1990, **423**.
5. Sweet, G. E. and Bell, J. P., *Text. Res. J.*, 1976, **46**(6), 447.
6. Chantrey, G. and Rattee, I. D., *J. Appl. Polym. Sci.*, 1974, **18**, 93.
7. McGregor, R., Peters, R. H. and Ramachandran, C. R., *J. Soc. Dyers Colour*, 1968, **84**, 9.
8. Hossain, T. M. A., Maeda, H., Iijima, T. and Morita, Z., *J. Pol. Sci., Polym. Lett.*, 1967, **5**, 1069.
9. Shibusawa, T., *J. Polym. Sci., Polym. Phys., Part B*, 1993, **31**, 29.
10. Hori, T., Fujita, I. and Shimizu, T., *J. Soc. Dyers Colour*, 1986, **102**, 181.
11. Hann, R. A. and Beck, N. C., *J. Imaging Technol.*, 1990, **16**, 238.
12. Hann, R. A., unpublished results.
13. Shinozaki, K. and Hirano, H., *J. Imaging Sci. Technol.*, 1994, **38**(6), 571.
14. Shearmur, T. E., Drew, D. W., Clough, A. S., van der Grinten, M. G. D. and Slark, A. T., submitted to *Polymer*.
15. Slark, A. T., *Eur. Polym. J.*, (submitted).
16. Slark, A. T., *Polymer*, (submitted).
17. Fedors, R. F., *Polym. Eng. Sci.*, 1974, **14**, 147.
18. Van Krevelen, D. W., *Properties of Polymers*. Elsevier, Amsterdam, 1986.
19. de Naylor, T., in *Comprehensive Polymer Science*, ed. G. Allen and J. C. Bevington, Vol. 2, Pergamon Press, Oxford, 1989.
20. Barrer, R. M., *J. Phys. Chem.*, 1957, **61**, 178.
21. Meares, P., *J. Am. Chem. Soc.*, 1954, **76**, 3415.
22. Brandt, W. W., *J. Phys. Chem.*, 1959, **63**, 1080.
23. DiBeneditto, A. T., *J. Polym. Sci.*, 1963, **A1**, 3459.
24. Paul, D. R. and DiBeneditto, A. T., *J. Polym. Sci.*, 1964, **A2**, 1001.
25. Pace, R. J. and Datyner, A. J., *J. Polym. Sci., Polym. Phys. Ed.*, 1979, **17**, 437, 453, 465, 1675.
26. Pace, R. J. and Datyner, A. J., *J. Polym. Sci., Polym. Phys. Ed.*, 1980, **18**, 1103.
27. Bueche, F., *J. Chem. Phys.*, 1953, **21**, 1850.
28. Ferry, J. D., *Viscoelastic Properties of Polymers*, 2nd edn. Wiley, New York, 1970.
29. Fujita, H., Kishimoto, A. and Matsumoto, K., *Trans. Faraday Soc.*, 1960, **56**, 424.
30. Cohen, M. H. and Turnbull, D., *J. Chem. Phys.*, 1959, **31**, 1164.
31. Vrentas, J. S. and Duda, J. L., *J. Polym. Sci., Polym. Phys. Ed.*, 1977, **15**, 403.
32. Mauritz, K. A., Storey, R. F. and George, S. E., *Macromolecules*, 1990, **23**, 441.
33. Mauritz, K. A. and Storey, R. F., *Macromolecules*, 1990, **23**, 2033.
34. Zhang, J. and Wang, B. H., *Macromolecules*, 1987, **20**, 683.
35. Zhang, J. and Wang, B. H., *Macromolecules*, 1987, **20**, 2296.
36. Williams, M. L., Landel, R. F. and Ferry, J. D., *J. Am. Chem. Soc.*, 1955, **77**, 3701.
37. Ehlich, D. and Sillescu, H., *Macromolecules*, 1990, **23**, 1600.
38. Xia, J. L., Wang, C. H. and Li, B. Y., *Macromolecules*, 1990, **23**, 2739.
39. Kim, H., Waldow, D. A., Han, C. C., Tran Cong, Q. and Yamamoto, M., *Polym. Commun.*, 1991, **32**(4), 108.
40. Byers, G. W., *Macromolecules*, 1993, **26**, 4242.
41. Coleman, M. M., Graf, J. F. and Painter, P. C., *Specific Interactions and the Miscibility of Polymer Blends*, Technomic, 1991.
42. Barton, A., *Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Florida, 1983.