

# The effect of intermolecular forces on the glass transition of solute–polymer blends

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The effects of dye–polymer interactions on the  $T_g$  of dye–polymer blends have been investigated using a disazothiophene dye solute in a variety of polymer structures. The dye was found to decrease the  $T_g$  of some polymers (plasticization) while increasing the  $T_g$  of others (antiplasticization). The  $T_g$  of a dye–polymer blend depended on the polymer  $T_g$ , the dye solute  $T_g$ , their relative concentrations and dye–polymer affinity. Increasing dye–polymer affinity produced stronger interaction between the dye and polymer, leading to higher  $T_g$  of the dye–polymer blend. Excellent correlations were established between  $T_g$  enhancement and the dye–polymer solubility parameter match which was used to predict dye–polymer affinity. Solubility parameters indicated that the combination of polar and hydrogen bonding forces controlled the elevation of  $T_g$ , since the best correlation was obtained by neglecting dispersion forces. © 1997 Elsevier Science Ltd.

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## INTRODUCTION

The behaviour of solutes in polymers is important for many industrial applications. A wide variety of additives are incorporated in polymers including plasticizers, antiplasticizers, processing aids, lubricants and heat stabilizers<sup>1</sup>. Additionally, highly functional organic molecules are incorporated in polymers such as pharmaceuticals in drug delivery systems<sup>2</sup> and dyes for textiles or film images<sup>3</sup>. Dye molecules usually have molecular weights in the range 200–500 g mol<sup>-1</sup>, with a size which is two to five times that of a typical polymer repeating unit. Such large molecules will exhibit a substantial change in diffusion coefficient at  $T_g$  because the size of the solute dictates that transport is coupled with the cooperative relaxation associated with the glass transition<sup>4</sup>. For example, in a publication related to this work it has been illustrated that the release of dye from various donor dye–polymer blends to an acceptor polymer matrix is controlled by the glass transition of the dye–polymer blend<sup>5</sup>. The  $T_g$  of the dye–polymer blend was shown to be the critical parameter for the transport of four different dyes from a wide variety of polymer matrices. The variation in  $T_g$  of these blends suggested that dye–polymer affinity could be an important factor.

It is well known that copolymers or polymer blends can give rise to glass transition temperatures significantly higher than expected, resulting from intermolecular interactions. Examples include poly[vinylidene chloride-co-(meth)acrylates]<sup>6</sup>, poly(vinylidene chloride-co-acrylonitrile)<sup>7</sup>, poly(*N*-vinyl pyrrolidone-co-acrylic acid)<sup>8</sup>, blends of poly(4-vinyl pyridine) with poly(4-hydroxystyrene)<sup>9</sup>, blends of poly(acrylic acid) with poly(vinyl methyl ether)<sup>10</sup> and blends of poly(*N*-ethylcarbazol methyl methacrylate) with poly(dinitrobenzoyloxy ethyl

methacrylate)<sup>11–13</sup>. In all of these systems the  $T_g$  is elevated as a result of relatively strong interactions between electron donating and electron accepting functional groups on separate components. The glass transitions of polymer–polymer blends have been reported extensively and there are a number of equations relating the glass transition of a polymer blend to its composition. These equations include those of Fox<sup>14</sup>, Kelly–Bueche<sup>15</sup>, Couchman–Karasz<sup>16</sup>, Gordon–Taylor<sup>17</sup> and Kwei<sup>18</sup>. The last includes a factor which accounts for the increase in  $T_g$  resulting from interactions between the two components.

Although usually applied to polymer–polymer blends, these expressions can also be applied to copolymers and also solute–polymer blends. More recently, Painter *et al.*<sup>19</sup> have identified a more sophisticated equation according to both intermolecular interactions between two components and self-association of one component. A simplified form of this equation results in an expression similar to the Kwei equation.

The purpose of this publication is to report investigations into factors influencing the magnitude of the glass transition of dye solute–polymer blends, especially the effects of intermolecular forces and dye–polymer affinity for a particular dye solute in a range of polymer structures.

## EXPERIMENTAL

### Materials

The dye molecule studied in this work was a disazothiophene molecule, used as supplied by Zeneca Specialists and illustrated in *Figure 1*. It should be noted that the dye contains a stiff central conjugated aromatic structure to which various functional groups are attached. Functional groups which contain lone pairs

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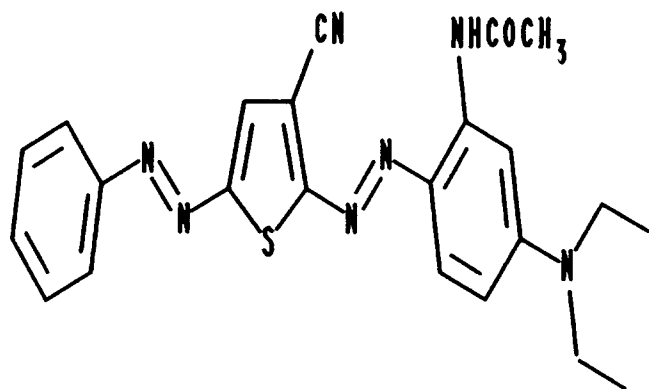
of electrons are an integral part of, or are bonded directly to, the aromatic core. The various polymers investigated are listed in *Table 1* and these were used as obtained from the various suppliers. The polymers were deliberately chosen to be amorphous in order to simplify the analysis of results.

#### Formation of dye–polymer blends

Dyes and polymers were dissolved in tetrahydrofuran (THF) with a total solids content of 6.75 wt% and a dye/polymer ratio of 1 : 2 (w/w). The blends were coated on to a 3.5  $\mu\text{m}$  polyester [poly(ethylene terephthalate), PET] substrate using wire bars, and the evaporation of THF was encouraged using a hot hair dryer. The thickness of solution coated was only 36  $\mu\text{m}$ , producing a solid state dye–polymer film thickness of only 2.5  $\mu\text{m}$  after removal of solvent. Coatings were further dried and analysed by head space gas chromatography using a Perkin-Elmer Sigma 2000 gas chromatograph to determine the quantity of residual THF. It was found that post-heating of the coated film for 30 s at 110°C was necessary for effective solvent removal (THF < 0.05  $\mu\text{g cm}^{-2}$ ). All films were assessed using optical microscopy, prior to evaluation, to establish that no undissolved dye particles or crystals were present.

#### Determination of $T_g$ of dye–polymer blend coatings

A Perkin-Elmer DSC-4 instrument was used to



**Figure 1** Structure of the disazo thiophene dye molecule used in this work, showing the electron donating functional groups attached directly to, or within, the central conjugated aromatic structure

characterize transitions in the dyecoat layers studied, using an indium standard for calibration and a heating rate of 20°C min<sup>-1</sup>. In the conventional use of differential scanning calorimetry (d.s.c.) for solid polymer powders or chips, the material is usually heated to high temperature and rapidly cooled to give the samples the same thermal history<sup>20</sup>. The  $T_g$  is then determined from the second run, and this was the method used to determine the glass transitions of the polymers used in the donor matrix (*Table 1*). However, for dye–polymer blends,  $T_g$  measurements were made during the first run to prevent morphology changes affecting the results. Dye–donor polymer mixtures were coated as detailed previously. An identical area of polyester base without dye–polymer coating, which had received the same thermal treatment, was used as a reference. The software subtracted the reference from the sample to provide the  $T_g$  of the dye–polymer coating.

#### Solubility parameters as a guide for dye–polymer affinity

Group molar attraction constants and group contributions to molar volume were determined, allowing solubility parameters to be calculated for any molecule from their constituent functional groups since

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

where  $E$  is the molar attraction constant for a particular functional group with volume  $V$ <sup>21</sup>. Maximum compatibility will be achieved if the solubility parameters of the two components are identical. For components 1 and 2 a measure of the compatibility is given by the quantity  $(\delta_1 - \delta_2)^2$ . Several attempts have been made to dissect the solubility parameter, including splitting into non-polar and polar contributions. One notable attempt is to assume that the cohesive energy is made up of a linear combination of contributions from non-polar/dispersion forces, polar interactions and hydrogen bonding interactions:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2)$$

where  $\delta$  is the global solubility parameter and  $\delta_d$ ,  $\delta_p$  and  $\delta_h$  are the solubility parameters resulting from dispersion, polar and hydrogen bonding forces, respectively. Hansen<sup>22,23</sup> proposed extension of the Hildebrand theory to polar and hydrogen bonding forces in this fashion and

**Table 1** Description of polymers used for blending with disazo thiophene dye

| Polymer type                                  | Supplier              | $T_g$ (°C) | Abbreviation |
|---|-----------------------|------------|--------------|
| Ethyl cellulose                               | Hercules              | 93.0       | EC           |
| Polystyrene                                   | Polysciences          | 104.5      | PS           |
| Poly(styrene-co-acrylonitrile) <sup>a</sup>   | Polysciences          | 103.0      | SAN          |
| Poly( <i>p</i> -hydroxy styrene)              | Maruzen Petrochemical | 145.0      | PPHS         |
| Chlorinated poly(vinyl chloride) <sup>b</sup> | Zeneca Resins         | 99.0       | CPVC         |
| Poly(vinyl butyral) <sup>c</sup>              | Sekisui Chemical      | 85.0       | PVB          |
| Poly(vinyl aceto acetal) <sup>d</sup>         | Sekisui Chemical      | 96.0       | PVAA         |
| Poly(vinyl formal) <sup>e</sup>               | Monsanto              | 86.5       | PVF          |
| Polyurethane                                  | B. F. Goodrich        | 22.0       | PU           |

<sup>a</sup> Contains 3 : 1 (w/w) styrene/acrylonitrile

<sup>b</sup> 50% of the vinyl chloride units are chlorinated, producing effectively a 1 : 1 copolymer of vinyl chloride and 1,2-dichloroethene

<sup>c</sup> Terpolymer containing 3% vinyl acetate, 33% vinyl alcohol and 64% vinyl butyral

<sup>d</sup> Terpolymer containing 3% vinyl acetate, 27% vinyl alcohol and 70% vinyl acetal

<sup>e</sup> Terpolymer containing 13% vinyl acetate, 7% vinyl alcohol and 80% vinyl formal

defined parameter group contributions for the separate forces as follows:

$$\delta_d = \frac{\sum F_{di}}{V} \quad (3)$$

$$\delta_p = \frac{\sqrt{(\sum F_{pi}^2)}}{V} \quad (4)$$

$$\delta_h = \sqrt{\left(\frac{\sum E_{hi}}{V}\right)} \quad (5)$$

where  $F_{di}$ ,  $F_{pi}$  and  $E_{hi}$  are the group contributions for dispersion, polar and hydrogen bonding forces, respectively. These component solubility parameters for dye and polymers were calculated from group contributions for the dye molecule and the polymer average repeating unit, using the values compiled by Van Krevelen<sup>21</sup>.

## RESULTS AND DISCUSSION

### The $T_g$ of solute–polymer blends

The glass transition temperatures of the polymers, which were determined experimentally ( $T_{g\text{pol}}$ ), and their respective dye–polymer blends ( $T_{g\text{exp}}$ ), are shown in Table 2. Inclusion of the dye in several of the polymer matrices (EC, PS, PPHS, SAN and CPVC) causes depression of  $T_g$ , or plasticization. However, for several dye–polymer combinations (PVB, PVAA and PVF), the inclusion of the dye solute causes an increase in the  $T_g$  when compared to the polymer itself, i.e. antiplasticization. Therefore, for similar polymer  $T_g$  the inclusion of solute causes depression of  $T_g$  in some cases, but elevation of  $T_g$  in others. The plasticization effect observed in several polymers is a common feature of the inclusion of solutes in polymers<sup>1</sup>. However, the elevation of  $T_g$  in certain matrices is an unexpected result since ‘antiplasticization’ is usually associated with hindering the molecular motions associated with the sub- $T_g$   $\beta$ -relaxations (involving small polymer segments) and not the co-operative  $\alpha$ - $T_g$  (involving a number of polymer repeating units). Antiplasticizers normally lower the glass transition temperature, but enhance mechanical properties by either suppressing the intensity of the  $\beta$ -relaxation or altering the temperature at which

it occurs, resulting from solute–polymer interactions. Such behaviour has been illustrated for diphenyl hydrazone, phthalate and succinate solutes in polycarbonate<sup>24–26</sup>, cholesterol compounds in poly(butyl methacrylate)<sup>27</sup> and an aromatic ether solute in poly-(bisphenol A, 2-hydroxypropyl ether)<sup>28</sup>. However, it is clear that in the case reported here, the cooperative motion associated with  $T_g$  can be hindered by the presence of the dye solute causing the  $T_g$  to increase. The antiplasticization effect is relatively small for those polymers listed in Table 2. This was investigated further using a polyurethane with a low  $T_g$  (22°C). A large antiplasticization effect was observed in this case since the  $T_g$  of the polymer was elevated to 38°C in the dye–polymer blend (not shown in Table 2).

### Factors influencing $T_g$ of dye–polymer mixtures

The solute–polymer  $T_g$  values obtained have been used to test a simple model illustrated in Figure 2. In this model, the actual solute–polymer  $T_g$  depends on the polymer  $T_g$  (defined by its structural characteristics), the solute  $T_g$  (defined by its structural characteristics), the concentration of solute and the solute–polymer interaction. For the addition of diluents to polymers, the  $T_g$  of a mixture can be given by the Fox equation<sup>14</sup>:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (6)$$

where  $T_g$  is the glass transition of a mixture of polymer 1 with diluent 2,  $w_1$  is the weight fraction of polymer with glass transition  $T_{g1}$  and  $w_2$  is the weight fraction of diluent 2 with glass transition  $T_{g2}$ . The Fox equation neglects intermolecular forces. The Fox equation was applied to the dye–polymer systems, using the dye–EC combination as a reference point. EC produced the lowest  $T_g$  values, suggesting that the dye–polymer interactions were weakest for this particular combination. For the dye–EC combination, it was assumed that the calculated  $T_g$  ( $T_{g\text{calc}}$ ) was equal to the experimentally determined  $T_g$  ( $T_{g\text{exp}}$ ) in order to calculate dye  $T_g$  from equation (6); then using this dye  $T_g$ ,  $T_{g\text{calc}}$  was determined for the other polymers using equation (6) (see Table 2). The experimental  $T_g$  was generally higher than the calculated  $T_g$  and this difference was then correlated with dye–polymer affinity.

**Table 2** Comparison of  $T_{g\text{pol}}$ ,  $T_{g\text{exp}}$ ,  $T_{g\text{calc}}$ ,  $\delta T_g$  and  $\Delta T_g$  for various dye–polymer blends

| Polymer | $T_{g\text{pol}}^a$ (°C) | $T_{g\text{exp}}^b$ (°C) | $T_{g\text{calc}}^c$ (°C) | $\delta T_g^d$ (°C) | $\Delta T_g^e$ |
|---------|--------------------------|--------------------------|---------------------------|---------------------|----------------|
| EC      | 93.0                     | 85.0                     | 85.0                      | 0                   | 0              |
| PS      | 104.5                    | 95.0                     | 92.4                      | 2.6                 | 21.5           |
| PPHS    | 145.0                    | 122.0                    | 116.8                     | 5.2                 | 18.4           |
| SAN     | 103.0                    | 97.0                     | 91.4                      | 5.6                 | 48.3           |
| CPVC    | 99.0                     | 97.0                     | 88.9                      | 8.1                 | 80.2           |
| PVB     | 85.0                     | 88.5                     | 79.0                      | 8.6                 | 169.0          |
| PVF     | 86.5                     | 91.5                     | 80.9                      | 10.6                | 189.0          |
| PVAA    | 96.0                     | 98.0                     | 87.0                      | 11.0                | 122.0          |

<sup>a</sup> Polymer glass transition temperature experimentally determined

<sup>b</sup> Glass transition temperature of the dye–polymer blend experimentally determined

<sup>c</sup> Glass transition temperature of the dye–polymer blend calculated using the Fox equation

<sup>d</sup>  $\delta T_g = T_{g\text{exp}} - T_{g\text{calc}}$

<sup>e</sup>  $\Delta T_g = \frac{(T_{g\text{exp}} - T_{g\text{calc}})}{(T_{g\text{pol}} - T_{g\text{calc}})} \times 100$

Two other parameters were then defined relating to the difference between experimental and calculated  $T_g$ :

$$\delta T_g = T_{g\text{exp}} - T_{g\text{calc}} \quad (7)$$

$$\Delta T_g = \frac{(T_{g\text{exp}} - T_{g\text{calc}})}{(T_{g\text{pol}} - T_{g\text{calc}})} \times 100 \quad (8)$$

Equation (8) attempts to normalize for differences in the polymer  $T_g$  ( $T_{g\text{pol}}$ ) since the magnitude of  $\delta T_g$  will depend on the polymer  $T_g$ . The use of the Fox equation requires knowledge of the  $T_g$  of a dye molecule which is usually highly crystalline in its pure state. This raises questions about the validity of the concept of a low molecular weight crystalline molecule having a glass transition. However, it must be emphasized that the solid dye-polymer blends are prepared by rapidly evaporating THF from thin film coatings. The transformation from dye-polymer in solution to the solid state occurs rapidly ( $< 1$  s). This is thought to produce a solid solution of dye in polymer with the dye being dispersed at a molecular level in the polymer matrix, thereby interacting with polymer chains and affecting the solid state properties. The absence of dye crystals in the film, the observation of a single  $T_g$  for the dye-polymer blends and the modification of polymer  $T_g$  by the presence of the dye all suggest that the dye is mixed with the polymers on a molecular level so that it can solvate polymer chains. This suggests that the film preparation creates a glassy

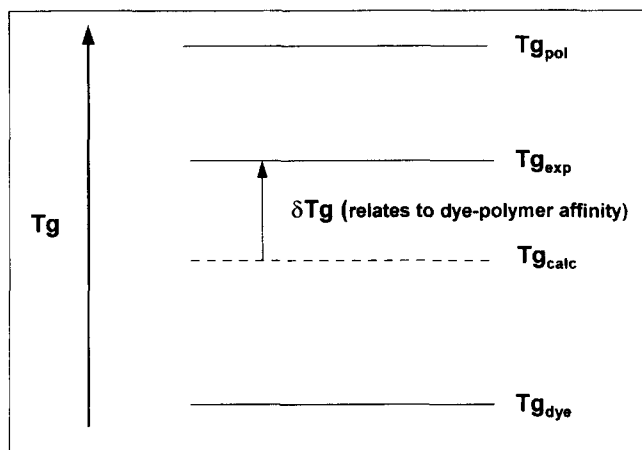


Figure 2 Overall simple model of factors influencing the  $T_g$  of solute-polymer blends

dye-polymer blend where the matrix is strongly influenced by the presence of the dye. In this state, there is no apparent reason why the dye molecule cannot behave as if it were a coloured conventional amorphous plasticizer.

Using EC as a reference point, the dye  $T_g$  was calculated to be  $70^\circ\text{C}$ . For the various dye-polymer combinations,  $T_{g\text{calc}}$ ,  $T_{g\text{exp}}$ ,  $\delta T_g$  and  $\Delta T_g$  are given in Table 2;  $\delta T_g$  are zero for the dye-EC reference combination. For all of the other polymers,  $\delta T_g$  and  $\Delta T_g$  are consistently positive. The value of  $\delta T_g$  is low for PS since the main point of interaction with the dye is likely to be the relatively weak phenyl group. The magnitude of  $\delta T_g$  increases with the inclusion of the more polar cyano group in SAN and also for materials containing chloro (CPVC), ether (PVAA and PVF) and hydroxyl (PPHS, PVAA and PVF). From a qualitative viewpoint, the  $T_g$  appears to increase as the general polarity and hydrogen bonding character of the polymer increases.

#### Determination of solute $T_g$

It can be deduced that the dye  $T_g$  must lie between  $22$  and  $105^\circ\text{C}$ , since the dye causes the  $T_g$  of CPVC to decrease whilst causing the  $T_g$  of PU to rise. The accuracy of the dye  $T_g$  predicted from the dye-EC reference point was investigated using d.s.c. Crystalline disazothiophene dye was heated above its melting point ( $210^\circ\text{C}$ ) to  $225^\circ\text{C}$  and supercooled to room temperature at a rate of  $200^\circ\text{C min}^{-1}$ . A second run of the sample was then taken and a glass transition for the dye was observed at  $68^\circ\text{C}$ . This  $T_g$  is very similar to the  $T_g$  of  $70^\circ\text{C}$  predicted from the dye-EC combination using the Fox equation, thereby vindicating the previous assumptions.

#### Quantifying the dye-polymer interaction and its effect on $T_g$

Table 3 shows the calculations of  $\delta$ ,  $\delta_d$ ,  $\delta_p$  and  $\delta_h$  for all polymers used in addition to the disazothiophene dye. The relationship between  $\Delta T_g$  and the global solubility parameter difference between dye and polymer is illustrated in Figure 3. The data are very scattered and the correlation is poor. Attempts were also made to correlate  $\Delta T_g$  separately with the differences in dispersion and polar and hydrogen bonding solubility parameters between dye and polymer. The data are not illustrated, but the correlations were equally poor. Various combinations of the Hansen solubility approach

Table 3 Calculated solubility parameters for dye and polymers

| Material | $\delta^a$ ( $\text{J cm}^{-3}$ ) <sup>1/2</sup> | $\delta_d^b$ ( $\text{J cm}^{-3}$ ) <sup>1/2</sup> | $\delta_p^c$ ( $\text{J cm}^{-3}$ ) <sup>1/2</sup> | $\delta_h^d$ ( $\text{J cm}^{-3}$ ) <sup>1/2</sup> | $\delta_{ph}^e$ ( $\text{J cm}^{-3}$ ) <sup>1/2</sup> |
|----------|--|--|--|--|---|
| Dye      | 21.32  | 17.30  | 7.63   | 9.86   | 12.47   |
| PS       | 18.20  | 18.16  | 1.12   | 0.00   | 1.12  |
| PPHS     | 23.59  | 18.21  | 5.09   | 14.11  | 15.00   |
| SAN      | 19.97  | 17.93  | 7.74   | 4.18   | 8.80  |
| CPVC     | 20.40  | 17.90  | 9.17   | 3.40   | 9.78  |
| PVB      | 18.42  | 14.51  | 4.51   | 10.42  | 11.35   |
| PVAA     | 18.07  | 13.72  | 5.36   | 10.47  | 11.76   |
| PVF      | 17.75  | 13.90  | 5.83   | 9.37   | 11.04   |

<sup>a</sup> Global solubility parameter

<sup>b</sup> Dispersion component solubility parameter

<sup>c</sup> Polarity component solubility parameter

<sup>d</sup> Hydrogen bonding component solubility parameter

<sup>e</sup> Average polar/hydrogen bonding solubility parameter

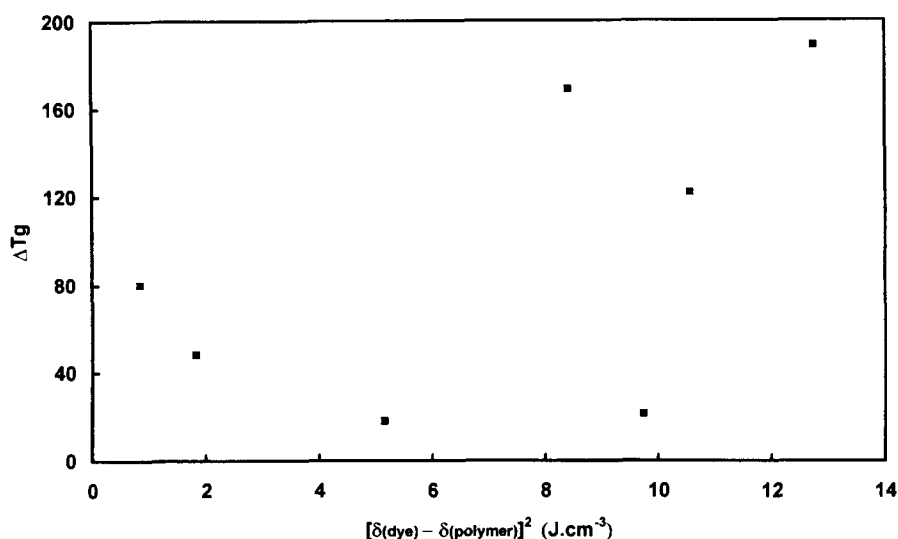


Figure 3 Relationship between  $\Delta T_g$  and the difference in global solubility parameter between dye and polymers

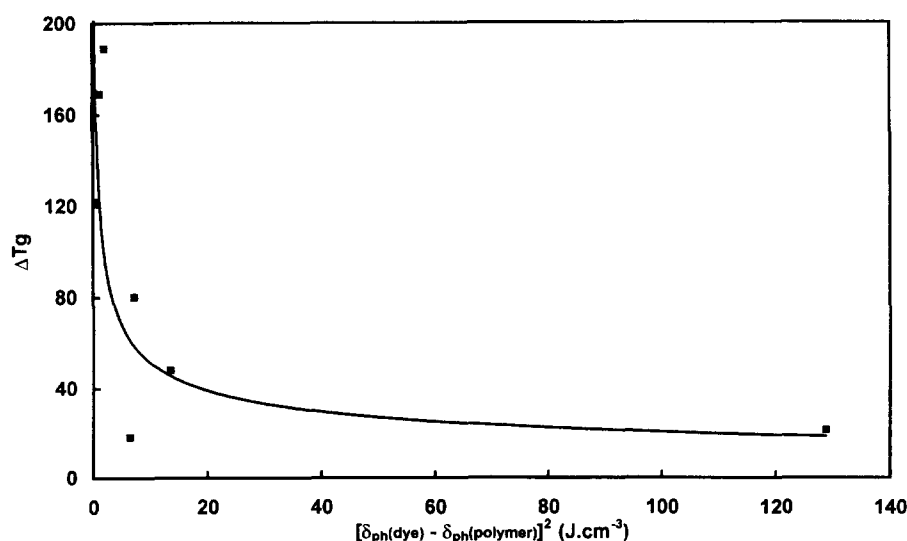


Figure 4 Relationship between  $\Delta T_g$  and the difference in average polar/hydrogen bonding solubility parameter between dye and polymers

were investigated and the most successful attempt was to combine the polar hydrogen bonding components as one parameter ( $\delta_{ph}$ ), i.e.

$$\delta_{ph}^2 = \delta_p^2 + \delta_h^2 \quad (9)$$

Table 3 also includes the data for the various materials calculated according to equation (9). Using this approach, it should be emphasized that the dispersion components are ignored. Figure 4 illustrates the relationship between  $\Delta T_g$  and the difference in averaged polar/H-bonding solubility parameters between the dye and the various polymers. The correlation is now reasonable. The data suggest that higher blend  $T_g$  values are obtained when there is greater dye-polymer affinity and a closer match between dye and polymer solubility parameters. However, on closer inspection of Figure 4, there is a peak in the data where the solubility parameters of dye and polymer tend towards equality, suggesting that this relationship does not hold in all cases. For further investigation, the  $\Delta T_g$  data were plotted against  $\delta_{ph}$  for the polymer only (ignoring the  $\delta_{ph}$  for the dye) and these data are reproduced in Figure 5.

For low values of  $\delta_{ph}$ ,  $\Delta T_g$  is low. As  $\delta_{ph}$  increases,  $\Delta T_g$  rises, peaks at a maximum value and then falls to a low value. The appearance of this result is qualitatively identical to the determination of polymer solubility parameters by swelling measurements in solvents of different solubility parameter<sup>21</sup>. The amount of solvent depends on the solubility parameter of the solvent with maximum swelling occurring when the solubility parameters of solvent and polymer are equal. If enhanced dye-polymer affinity results in higher  $T_g$ , then the peak position should define the point at which the solubility parameters of the dye solute and polymer matrix are equal. Extrapolation of this peak results in a dye  $\delta_{ph}$  value of  $10.9 \text{ (J cm}^{-3}\text{)}^{1/2}$ , which is different to the value of  $12.47 \text{ (J cm}^{-3}\text{)}^{1/2}$  in Table 3 calculated from group contributions. This suggests that the calculation of the dye solubility parameter from groups' contributions is subject to error. This may not be surprising since the number and type of functional groups listed for the calculation of  $\delta_{ph}$ <sup>21</sup> are limited with respect to dye structures, and several assumptions are required to establish the dye solubility parameter.

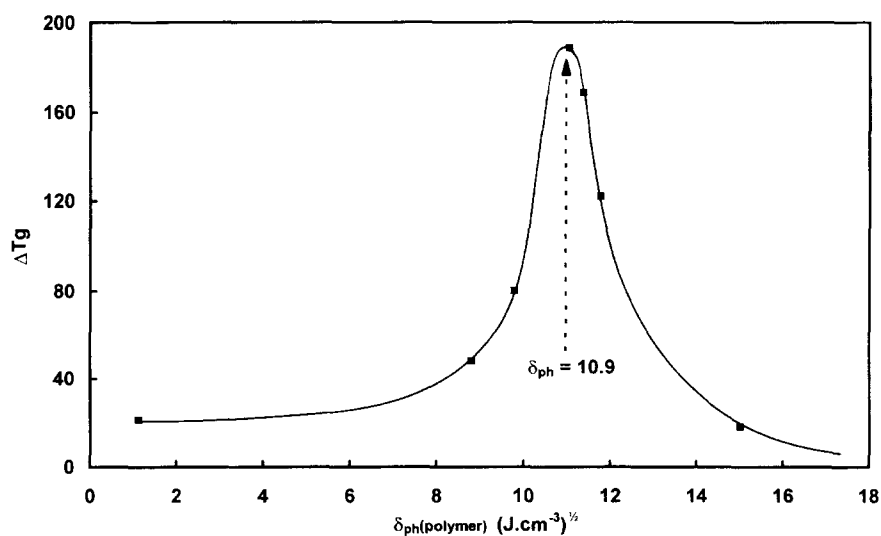


Figure 5 Relationship between  $\Delta T_g$  and the average polar/hydrogen bonding solubility parameter of the polymers, neglecting the dye

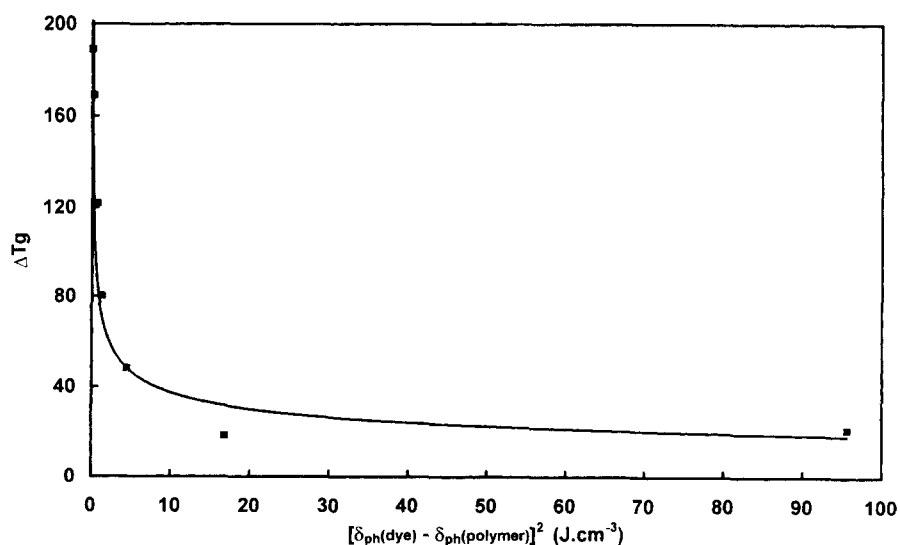


Figure 6 Relationship between  $\Delta T_g$  and the difference in average polar/hydrogen bonding solubility parameter between dye and polymers, using Figure 5 to determine the dye solubility at maximum  $\Delta T_g$

The data used in Figure 4 are replotted in Figure 6, but using the solubility parameter of the dye obtained from the peak maximum in Figure 5, assuming that the maximum  $T_g$  occurs when the solubility parameters of dye and polymer are equal. The relationship between  $\Delta T_g$  and dye-polymer solubility parameter difference is now excellent. The  $\Delta T_g$  is low when there is a large difference in dye-polymer affinity, but the elevation in  $T_g$  increases as dye-polymer affinity is enhanced and is highest when the solubility parameters of dye and polymer approach equality. There are some previous cases where plasticization phenomena have been related to solute-polymer affinity and solubility parameter differences. Investigating the effects of solute type on the plasticization of PET, Ingamells and Yanumet<sup>29</sup> showed that there was a relationship between  $T_g$  and dispersion component solubility parameter differences. For the effect of solute type on the plasticization of the more polar polyacrylonitrile (PAN), Ingamells<sup>30</sup> illustrated that there was a relationship between  $T_g$  and the difference in average polar and hydrogen bonding solubility parameters between PAN and solvent. It is

interesting to note that the latter use of solubility parameters is identical to that used in the work described in this paper. However, in both of the previous studies, matching solubility parameters and solute-polymer affinity was found to increase plasticization and decrease the  $T_g$ ; this is completely opposite to the trend displayed in our work reported here. The results for PET and PAN may be confused since the materials studied were semicrystalline polymers, and the effects of plasticizer on the disruption of crystallinity was not studied. It is possible that solutes with high affinity for the polymer could enhance the fraction of amorphous polymer, producing different amounts of amorphous polymer accessible for plasticization. In the studies on PET and PAN the molecular weights of the solutes are low in comparison with those of our study on the dye solute and this could cause differences in interaction behaviour. Additionally, the PET and PAN data could be confused by the method used to do the experiments where the solvents are required to diffuse into polymer films before measurements of  $T_g$  are made. The concentrations of solutes with higher affinity will be higher, making them

appear to be more effective at lowering  $T_g$ . The concentrations of solutes in the polymers which are poor solvents will be low and additionally they may not be molecularly dispersed and could be aggregated because of the low solute-polymer affinity. This would result in *apparently* poor plasticization.

In studies on polymer-polymer blends of poly(ethylene glycol) with cellulosic polymers, Sakellariou *et al.* found that small depressions in  $T_g$  occur when one of the components phase separates<sup>31,32</sup>. Therefore, *apparently* ineffective plasticization can be obtained from blends where solute-polymer interactions are low due to phase separation resulting from the incompatibility of components. It is important to emphasize that intimate contact between solute and polymer is necessary to elucidate correctly mechanisms of interaction, and the method used in our work again should be highlighted. We argue that the combination of solute and polymer in a mutually good solvent followed by very rapid removal of a volatile solvent means that equal quantities of solutes can be dispersed at a molecular level, irrespective of solute-polymer affinity. It is believed that such a situation will lead to a more accurate description of the effects of intermolecular forces on  $T_g$ . Our results agree with the work of Kanig<sup>33</sup> on mixtures of polymer and plasticizer. He predicted that a good plasticizer is a poor solvent and that low affinity between plasticizer and polymer would result in efficient plasticization and low  $T_g$ . Conversely, a poor plasticizer is a good solvent, and high affinity between plasticizer and polymer results in higher  $T_g$ . Our results also agree with the examples cited earlier for copolymers or polymer blends where intermolecular interactions lead to increases in  $T_g$ <sup>6-13</sup>.

#### The use of solubility parameters

This study has shown that global solubility parameters do not predict differences in  $T_g$ . This contrasts with a previous study on dye diffusion in an amorphous polymer at high temperatures well above  $T_g$  where global solubility parameters were found to be useful in correlating dye transport with the solution-diffusion model of permeability<sup>34</sup>. However, the use of solubility parameters relating to polar and hydrogen bonding interactions is very useful in explaining differences in the glass transition of solute-polymer blends, provided that dispersion forces are ignored. Dispersion forces are relatively short range whereas polar and hydrogen bonding forces are longer range, suggesting that these longer range forces have more influence on the cooperative motions associated with the glass transition. The disazo thiophene dye has a molecular weight which is three to five times that of the polymer repeating units used. From a mechanistic viewpoint, the dye-polymer blend can be considered to be a three-dimensional network in which the dye solutes can behave as physical crosslinks, cooperatively interacting via polar and hydrogen bonding interactions with different polymer segments on the same chain or different polymer chains. This reduces the scope for the rotation of polymer segments about main chain bonds and causes an increase in the  $T_g$ .

#### CONCLUSIONS

The combination of a disazo thiophene dye molecule with a variety of polymer structures produced changes in the

glass transition. The polymer  $T_g$  decreased or increased depending on the magnitude of the  $T_g$  of the original polymer and the dye-polymer affinity. The former plasticization is typical of the addition of various diluents to polymers, whereas the latter antiplasticization is not.

The glass transition of the dye-polymer blend depended on the polymer  $T_g$ , the dye  $T_g$ , the relative dye/polymer concentrations and the dye-polymer interaction. The dye  $T_g$  was calculated using the dye-EC combination as a reference point and correlated very well with the experimentally determined value obtained via d.s.c. on an amorphous dye prepared by supercooling dye taken above its melting point. Dye-polymer blend  $T_g$  values were calculated using the Fox equation and compared to experimentally determined  $T_g$  values. In all cases the actual  $T_g$  was higher than the calculated  $T_g$ . This difference in glass transition was correlated with dye-polymer affinity, using solubility parameter differences between dye and polymer as a predictive tool. It was found that global solubility parameter differences and separate three-dimensional solubility parameter differences produced a poor correlation with  $T_g$ . Averaging polar and hydrogen bonding solubility parameters produced a good correlation between the elevation of  $T_g$  and enhanced dye-polymer affinity, suggesting that these longer range forces are more important in controlling  $T_g$ .

The variation of  $T_g$  with the polar/H-bonding solubility parameters of the polymers only produced a dumb-bell shaped relationship with a maximum  $T_g$  at a certain solubility parameter. This maximum was assumed to be the point of optimum dye-polymer affinity where dye and polymer parameters were equal. This value was different to that calculated for the dye from group contributions, suggesting that the latter was subject to error. Dye-polymer solubility parameter differences were recalculated and the repeated correlation of  $T_g$  with dye-polymer affinity was found to be excellent. It was shown that the dye-polymer  $T_g$  was lowest when the mismatch in dye-polymer affinity was greatest. The  $T_g$  increased as the dye-polymer affinity was enhanced, resulting in the highest  $T_g$  when the dye-polymer affinity was at a maximum.

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#### REFERENCES

1. Kern Sears, J. and Darby, J. R., *The Technology of Plasticizers*, John Wiley, New York, 1982.
2. Domb A. J., *Polymeric Site-specific Pharmacotherapy*, John Wiley, Chichester, UK, 1994.
3. Hann, R. A. and Beck, N. C., *J. Imag. Technol.* 1990, **16**, 238.
4. Fujita, H., in *Diffusion in Polymers* (eds J. Crank and G. S. Park), Academic Press, 1968, Ch. 3.
5. Slark, A. T., *Eur. Polym. J.* (submitted).
6. Wessling, R. A., *Polyvinylidene Chloride*, Gordon and Breach, 1977.
7. Johnston, N. W., *J. Macromol. Sci. Chem.* 1975, **A9**, 461.

8. Shih, J. S., Chuang, J. C. and Login, R. B., *Polym. Mat. Sci. Eng.*, 1992, **67**, 266.
9. Vivas de Mefahi, M. and Frechet, J. M. J., *Polymer* 1988, **29**, 477.
10. Cowie, J. M. G., Garay, M. T., Lath, D. and McEwen, I. J., *Br. Polym. J.*, 1989, **21**, 81.
11. Simmons, A. and Natahnson, A., *Macromolecules* 1992, **25**, 1272.
12. Simmons, A. and Natahnson, A., *Macromolecules* 1991, **24**, 3651.
13. Simmons, A. and Natahnson, A., *Macromolecules* 1990, **23**, 5127.
14. Fox, T. G., *Bull. Am. Phys. Soc.* 1956, **1**, 123.
15. Kelley, F. N. and Bueche, F., *J. Polym. Sci.* 1961, **50**, 549.
16. Couchman, P. R., *Macromolecules* 1978, **11**, 1156.
17. Gordon, M. and Taylor, J. S., *J. Appl. Chem.* 1952, **2**, 493.
18. Kwei, T. K., *J. Polym. Sci., Polym. Lett. Edn* 1984, **22**, 307.
19. Painter, P. C., Graf, J. F. and Coleman, M. M., *Macromolecules* 1991, **24**, 5630.
20. Turi, E., *Thermal Characterisation of Polymeric Materials*, Academic Press, 1981.
21. Van Krevelen, D. W., *Properties of Polymers*, Elsevier Science, 1986.
22. Hansen, C. M., *J. Paint Technol.* 1967, **39**, 104, 511.
23. Hansen, C. M., *Ind. Eng. Chem. Prod. Res. Dev.* 1969, **8**, 2.
24. Cais, R. E., Nozomi, M., Murakami, O., Saita, A., Kawai, M. and Miyake, A., *Res. Dev. Rev.—Mitsubishi Kasei Corp.* 1992, **6**, 68.
25. Belifiore, L. A., Henrichs, P. M. and Cooper, S. L., *Polymer* 1984, **25**, 452.
26. Belifiore, L. A., Henrichs, P. M., Massa, D. J., Zumbulyadis, N., Rothwell, W. P. and Cooper, S. L., *Macromolecules* 1983, **16**, 1744.
27. Desphande, D. D., Basu, C. and Pandya, M. V., *J. Macromol. Sci. Chem.* 1988, **A25**, 1071.
28. Stevenson, W. T. K., Garton, A. and Wiles, D. M., *J. Polym. Sci., Polym. Phys.* 1986, **24**, 717.
29. Ingamells, W. and Yanumet, M., *Br. Polym. J.* 1980, **12**, 12.
30. Ingamells, W., in *Solvents—Neglected Parameter, Solvents Symposium* (ed. G. Kakabadse), University of Manchester Institute of Science and Technology, Manchester, UK, 1977.
31. Sakellariou, P., Rowe, R. C. and White, E. F. T., *Int. J. Pharm.* 1986, **31**, 55.
32. Sakellariou, P., Rowe, R. C. and White, E. F. T., *J. Appl. Polym. Sci.* 1987, **34**, 2507.
33. Kanig, G., *Kolloid Zeit.*, 1963, **190**, 1.
34. Slark, A. T. and Fox, J. E., *Polymer* (submitted).