PII: S0032-3861(96)01047-6

The effect of intermolecular forces on the glass transition of solute–polymer blends: 2. Extension to different solutes

A. T. Slark*
ICI Imagedata, Brantham, Manningtree, Essex, CO11 1NL, UK
(Received 30 October 1996; revised 18 November 1996)

The effects of intermolecular forces on the glass transition temperature (T_g) of various dye solutes in numerous polymer matrices have been investigated. The T_gs of these dye–polymer blends were found to depend on the polymer T_g, the dye T_g, their relative concentrations and the dye–polymer affinity. Attempts have been made to correlate increases in T_g with dye–polymer affinity using solubility parameters as a predictive tool. Poor correlations were obtained using global solubility parameters. Excellent correlations were made between elevation in T_g and enhanced dye–polymer affinity using averaged polar/hydrogen bonding solubility parameters. For all dye solutes, the T_g was low when there was a large mismatch in solubility parameters, increased as dye and polymer became more compatible and was at a maximum when the solubility parameters of both components were equal. The results also indicate that longer range polar and hydrogen bonding forces have a controlling influence on T_g. © 1997 Elsevier Science Ltd.

(Keywords: solute; polymer; interactions)

INTRODUCTION

It is well known that copolymers or polymer blends can give rise to glass transition temperatures (T_gs) significantly higher than expected, resulting from intermolecular interactions. Examples include poly(vinylidene chloride-co-(meth)acrylates)[1], poly(vinylidene chloride-co-acrylonitrile)[2], poly(N-vinyl pyrrolidone-co-acrylic acid)[3], blends of poly(4-vinyl pyridine) with poly(4-hydroxystyrene)[4], blends of poly(acrylic acid) with poly(vinyl methyl ether)[5] and blends of poly(N-ethylcarbazol methyl methacrylate) with poly(dinitrobenzoyloxy ethyl methacrylate)[6–8]. 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 T_gs of polymer–polymer blends have been reported extensively, and there are a number of equations relating the T_g of a polymer blend to its composition. These equations include those of Fox[9], Kelly–Bueche[10], Couchman–Karasz[11], Gordon–Taylor[12] and Kwei[13]. The latter includes a factor which accounts for the increase in T_g resulting from interactions between the two components. More recently, Painter et al.[14] have identified a more sophisticated equation accounting for 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. Although usually applied to polymer–polymer blends, these expressions and principles can also be applied to copolymers and solute–polymer blends.

In a previous paper the effects of solute–polymer affinity on the T_gs of solute–polymer blends were investigated using a particular dye molecule in a range of polymers[15]. Glass transitions were usually higher than expected and this enhancement in T_g was correlated with dye–polymer affinity using solubility parameter differences between dye and polymer as a predictive tool. The solubility parameters for dye and polymers were calculated from group contributions for the dye molecule and the polymer average repeating unit. 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 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 polymer solubility parameters only was found to be excellent producing a dumb-bell shape giving a maximum T_g at a certain solubility parameter. The solubility parameter producing the maximum T_g was assumed to be the point of maximum dye–polymer affinity, i.e. dye solubility parameter equal to polymer at maximum T_g. This value was different to that calculated for the dye from group contributions, suggesting that the latter is 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 is the purpose of this publication to extend the study of these effects of dye–polymer affinity on the glass transition of solute–polymer blends to investigate

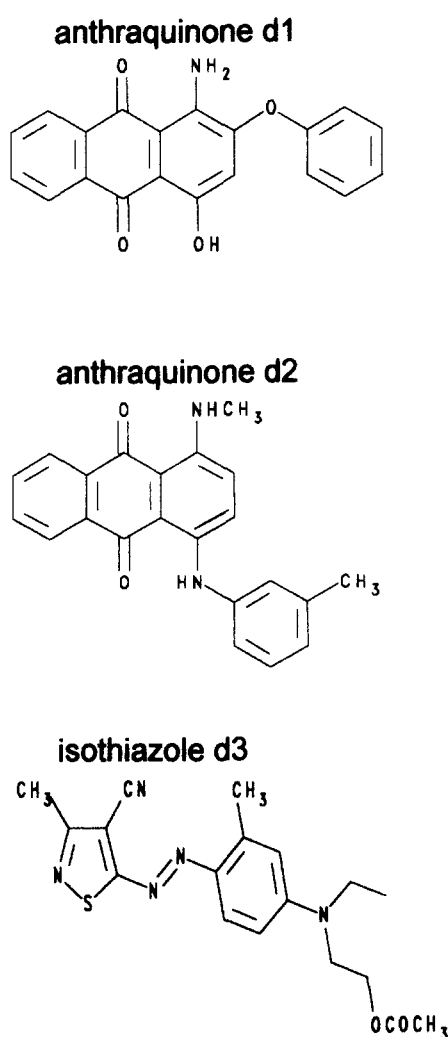* Current address: ICI Acrylics, PO Box 90, Wilton, Middlesbrough, Cleveland, TS90 8JE, UK

Figure 1 The structures of the various dye molecules used in this work

if the enhancement of T_g via higher solute–polymer affinity is universally applicable to different solutes.

METHOD

Materials

The dye molecules studied in this work were used as supplied by Zeneca Specialties and their structures are illustrated in *Figure 1*. It should be noted that these dyes

contain a stiff central conjugated aromatic structure to which various functional groups are attached. 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, with a variety of functional groups and T_gs.

Formation of dye–polymer blends

Dyes and polymers were dissolved in tetrahydrofuran (THF) solvent according to the following mixtures (all wt%): d1 anthraquinone magenta, dye 6.5%/polymer 5.9%/THF 91.0%; d2 anthraquinone cyan, dye 4.5%/polymer 4.5%/THF 91.0%; d3 isothiazole magenta, dye 3.0%/polymer 6.0%/THF 91.0%.

The blends were coated onto 3.5 μm polyester (poly(ethylene terephthalate), PET) substrate using wire bars and the evaporation of THF was encouraged using a hot hair dryer. It should be noted that solid-state dye–polymer coatings (thickness approximately 1 μm) were produced by rapidly evaporating solvent from homogeneous dye–polymer solutions. It should be noted that the transformation from dye and polymer in solution to dye–polymer solid state under these conditions is rapid, with the majority of THF evaporating in less that 1 s. 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 the coated film for 30 s at 110°C was necessary for effective solvent removal (THF < 0.05 μg 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_gs of dye–polymer blend coatings

A Perkin-Elmer DSC-4 instrument was used to characterize transitions in the dyecoat layers studied, using an indium standard for calibration and a heating rate of 20°C min^{-1}. 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[16]. 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 (*Table 1*). However, for dye–polymer blends a crystallization exotherm and a

Table 1 Polymers used to create dye–polymer blends

Polymer type	Supplier	T_g (°C)	Abbreviation
Phenoxy	Union Carbide	78.5	PHEN
Poly(vinyl chloride)	Polysciences	82.5	PVC
Poly(vinyl butyral)	Sekisui Chemical	85.0	PVB
Poly(vinyl formal)	Monsanto	86.5	PVF
Ethyl cellulose	Hercules	93.0	EC
Poly(vinyl aceto acetal)	Sekisui Chemical	96.0	PVAA
Chlorinated poly(vinyl chloride)	Zeneca Resins	99.0	CPVC
Polycarbonate	Dow Chemical	100.0	PC
Polyester	Dynamit Nobel	100.0	PEST
Poly(styrene-co-acrylonitrile)	Polysciences	103.0	SAN
Polystyrene	Polysciences	104.5	PS
Poly(p-hydroxy styrene)	Maruzen Petrochemical	145.0	PPHS

melting endotherm were found above T_g during the first temperature cycle. This was thought to be a result of dye mobility above T_g resulting in phase separation. Therefore, T_g measurements were made during the first run. Dye–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

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

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (1)$$

where δ is the global solubility parameter and δ_d, δ_p and δ_h are the solubility parameters resulting from dispersion, polar and hydrogen bonding forces, respectively. Hansen[17,18] proposed extension of the original Hildebrand theory to polar and hydrogen bonding forces[19] and defined parameter group contributions for the separate forces as follows:

$$\delta_d = \frac{\sum F_{di}}{V} \qquad (2)$$

$$\delta_p = \frac{\sqrt{(\sum F_{pi}^2)}}{V} \qquad (3)$$

$$\delta_h = \sqrt{\left(\frac{\sum E_{hi}}{V}\right)} \qquad (4)$$

where F_{di}, F_{pi} and E_{hi} are the group contributions for dispersion, polar and hydrogen bonding forces, respectively. These equations permit calculations of the separate contributions for a molecule from its constituent groups. The previous publication[15] on the correlation of T_g with dye–polymer affinity illustrated that polar and hydrogen bonding forces controlled the increase in T_g resulting from enhanced dye–polymer affinity. Best results were obtained by ignoring dispersion forces and combining the polar and hydrogen bonding components as one parameter (δ_{ph}), i.e.

$$\delta_{ph}^2 = \delta_p^2 + \delta_h^2 \qquad (5)$$

Using this approach, a measure of compatibility for components 1 and 2 is given by the quantity $(\delta_{ph(1)} - \delta_{ph(2)})^2$. Therefore δ_{ph} for dyes and polymers were calculated from group contributions for the whole dye molecules and the polymer average repeating units, using the values complied by Van Krevelen[20]. These calculated solubility parameters are illustrated in *Table 2*.

RESULTS AND DISCUSSION

Model used

The solute–polymer T_g values obtained have been used to test the model illustrated in *Figure 2* and previously established for the combination of a
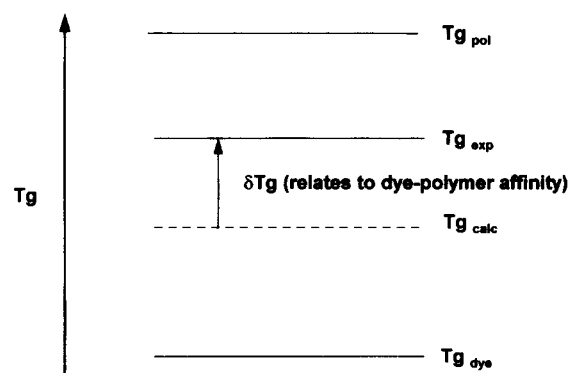

Figure 2 Overall simple model of factors influencing the T_g of solute–polymer blends

disazothiophene solute in various polymers[15]. In this model, the actual solute–polymer T_g depends on the polymer T_g (defined by its structural characteristics), the dye solute T_g (defined by its structural characteristics), the concentration of solute and the solute–polymer interaction. The T_g in the absence of interactions was calculated from the Fox equation[9],

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \qquad (6)$$

where T_g is the glass transition temperature of a mixture of polymer 1 with diluent 2, w_1 is the weight fraction of polymer with glass transition T_{g_1} and w_2 is the weight fraction of diluent 2 with glass transition T_{g_2}. 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. For a wide range of dye–polymer systems, 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 ($T_{g,calc}$) was equal to the experimentally determined T_g ($T_{g,exp}$) in order to calculate dye T_g from equation (6). Then using this dye T_g, $T_{g,calc}$ was determined for the other polymers using equation (6). The experimental T_g was generally higher than the calculated T_g and this difference was then correlated with dye–polymer affinity. Two other parameters were then defined relating to the difference between experimental and calculated T_g:

$$\delta T_g = T_{g,exp} - T_{g,calc} \qquad (7)$$

Table 2 Solubility parameters of dyes and polymers

Material	δ_p (J cm^{-3})$^{1/2}$	δ_h (J cm^{-3})$^{1/2}$	δ_{ph} (J cm^{-3})$^{1/2}$
Dye d1	5.14	11.85	12.92
Dye d2	4.03	5.99	7.22
Dye d3	7.44	10.17	12.60
PHEN	3.03	10.11	10.55
PVC	12.17	2.97	12.53
PVB	4.51	10.42	11.35
PVF	5.83	9.37	11.04
PVAA	5.36	10.47	11.76
CPVC	9.17	3.40	9.78
PC	3.01	6.80	7.44
PEST	3.04	7.78	8.35
SAN	7.74	4.18	8.80
PS	1.12	0.00	1.12
PPHS	5.09	14.11	15.00

$$\Delta T_g = \frac{(T_{g,\mathrm{exp}} - T_{g,\mathrm{calc}})}{(T_{g,\mathrm{pol}} - T_{g,\mathrm{calc}})} \times 100 \qquad (8)$$

Equation (8) attempts to normalize for differences in the polymer $T_g (T_{g,\mathrm{pol}})$ since the magnitude of δT_g will depend on the polymer T_g.

Solute 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 solid state occurs rapidly (< 1 s). This is thought to produce a solid solution of dye in polymer with the dye being molecularly dispersed in the polymer matrix, thereby interacting with polymer chains and affecting 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 they can solvate polymer chains. This suggests that the film preparation creates a glassy dye–polymer blend state where the matrix is strongly influenced by the presence of a dye which is molecularly dispersed. In this state, there is no apparent reason why the dye molecules cannot behave as if they were a coloured conventional amorphous plasticizers. The calculated T_g values for the various dyes are shown in *Table 3* and compared to the melting points of crystalline dye. The data suggest that the dyes have widely differing effects as plasticizers with T_gs ranging from 70 to $-55°C$. The plasticizing efficiencies of the dyes are very different. Dye d3 is an excellent plasticizer since its T_g is very low whereas dye d4 is a poor plasticizer. The previous study[15] showed that for certain dye–polymer combinations, dye d4 actually caused antiplasticization by increasing the polymer T_g. The order of dye T_g is equivalent to the order of the melting points. The ratio of T_g/T_m ranges from 0.55–0.71, with the average being 0.63. It is interesting to note that this average figure is similar to the empirical rule in polymer science that $T_g = \frac{2}{3} T_m$[20].

Dye–polymer blend T_g and the effect of the dye–polymer affinity

For the various dye–polymer combinations, $T_{g,\mathrm{calc}}$, $T_{g,\mathrm{exp}}$, δT_g and ΔT_g are given in *Tables 4–6*, for dyes d1, d2 and d3, respectively. Since EC is used as a reference point, both δT_g and ΔT_g are zero for the dye–EC combination. For most of the other polymers, δT_g is consistently positive. Form a qualitative viewpoint, the

Table 3 Thermal properties of dyes

Dye type	T_g (°C)	T_m (°C)	T_g (K)/T_m (K)
d1	17	185	0.63
d2	−3	127	0.68
d3	−55	120	0.56
d4[a]	70	210	0.71

[a] Disazothiophene dye molecule data from a previous publication[15]

Table 4 Thermal properties of d1–polymer blends

Polymer	$T_{g,\mathrm{pol}}$ (°C)	$T_{g,\mathrm{exp}}$ (°C)	$T_{g,\mathrm{calc}}$ (°C)	δT_g(°C)	ΔT_g
PHEN	78.5	61.0	43.3	17.7	50.3
PVC	82.5	60.0	44.9	15.1	40.2
PVB	85.0	–	–	–	–
PVF	86.5	67.0	46.4	20.6	51.4
EC	93.0	48.5	48.5	0.0	0.0
PVAA	96.0	65.0	50.0	15.0	32.6
CPVC	99.0	63.5	51.0	12.5	26.0
PC	100.0	61.5	51.3	10.2	20.9
PEST	100.0	61.0	51.3	9.7	19.9
SAN	103.0	63.5	52.4	1.1	21.9
PS	104.5	52.5	53.0	−0.5	−1.0
PPHS	145.0	–	–	–	–

Table 5 Thermal properties of d2–polymer blends

Polymer	$T_{g,\mathrm{pol}}$ (°C)	$T_{g,\mathrm{exp}}$ (°C)	$T_{g,\mathrm{calc}}$ (°C)	δT_g(°C)	ΔT_g
PHEN	78.5	–	–	–	–
PVC	82.5	–	–	–	–
PVB	85.0	61.0	35.5	25.5	51.8
PVF	86.5	65.5	35.8	29.7	58.9
EC	93.0	38.0	38.0	0.0	0.0
PVAA	96.0	72.0	39.2	32.8	57.7
CPVC	99.0	65.5	40.3	25.2	42.9
PC	100.0	–	–	–	–
PEST	100.0	–	–	–	–
SAN	103.0	64.0	41.7	22.3	36.4
PS	104.5	55.0	42.2	12.8	23.8
PPHS	145.0	80.0	55.5	25.0	27.4

Table 6 Thermal properties of d3–polymer blends

Polymer	$T_{g,\mathrm{pol}}$ (°C)	$T_{g,\mathrm{exp}}$ (°C)	$T_{g,\mathrm{calc}}$ (°C)	δT_g(°C)	ΔT_g
PHEN	78.5	46.0	19.7	26.3	44.7
PVC	82.5	41.5	21.6	19.9	32.7
PVB	85.0	–	–	–	–
PVF	86.5	47.5	23.4	24.1	38.2
EC	93.0	26.5	26.6	0.0	0.0
PVAA	96.0	52.0	27.7	24.3	35.6
CPVC	99.0	53.5	29.0	24.5	35.0
PC	100.0	45.5	29.5	16.0	22.5
PEST	100.0	45.0	29.5	15.5	22.0
SAN	103.0	54.0	30.8	23.2	32.1
PS	104.5	34.0	31.4	2.6	3.5
PPHS	145.0	–	–	–	–

T_g increases as the general polarity and hydrogen bonding character of the polymer increases. This would be expected to result in a stronger dye–polymer affinity. The value of δT_g is usually low for PS since the main point of interaction with the dye is likely to be the relatively weak phenyl group. This increases with the inclusion of the more polar cyano group (e.g. SAN) and materials containing chloro (e.g. CPVC), ether (e.g. PVAA and PVF) and hydroxyl (e.g. PPHS, PVAA and PVF). These materials are likely to produce stronger dye–polymer intermolecular forces.

Although the figures are not reproduced, the use of global solubility parameters was found to be unsatisfactory with correlations between T_g enhancement and solubility parameter being very scattered for all dyes d1, d2 and d3. This agrees with our previous work for a disazothiophene cyan dye. The relationships between ΔT_g and polymer δ_{ph} are illustrated in *Figures 3–5* for dye–polymer blends of dyes d1, d2 and d3, respectively.
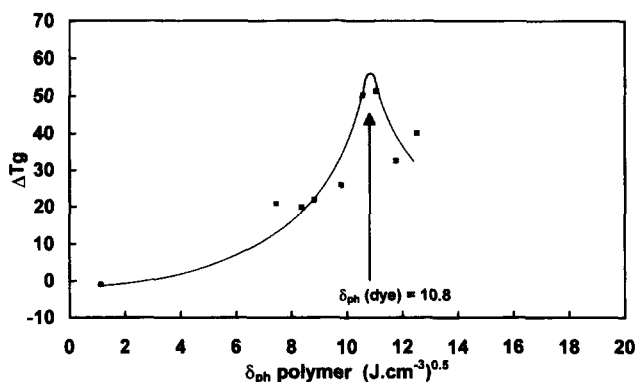
Figure 3 The variation of ΔT_g with polymer δ_{ph} for d1–polymer blends. The T_g is a maximum at a particular polymer solubility parameter equivalent to the dye
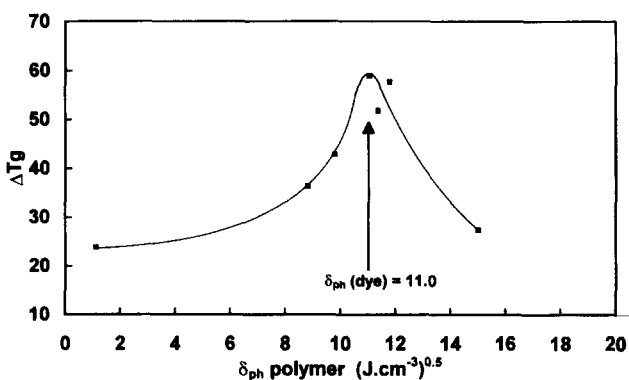

Figure 4 The variation of ΔT_g with polymer δ_{ph} for d2–polymer blends. The T_g is a maximum at a particular polymer solubility parameter equivalent to the dye
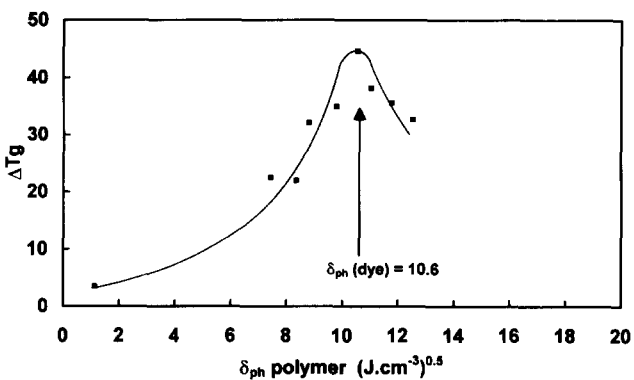

Figure 5 The variation of ΔT_g with polymer δ_{ph} for d3–polymer blends. The T_g is a maximum at a particular polymer solubility parameter equivalent to the dye
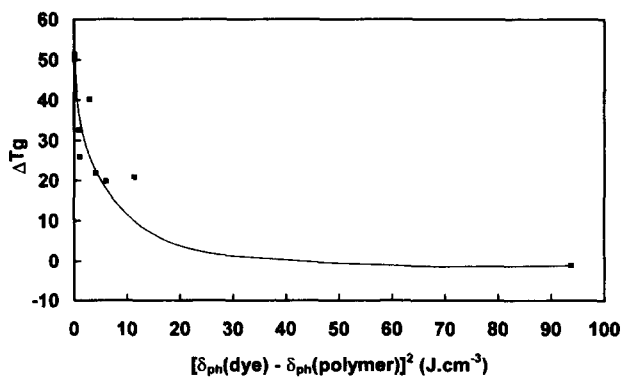

Figure 6 The variation of ΔT_g with dye–polymer solubility parameter difference for dye d1 blends

Table 7 Dye solubility parameters determined experimentally in comparison to solubility parameters calculated from group contributions

Dye type	Experimental δ_{ph} (J cm^{-3})$^{1/2}$ [a]	Calculated δ_{ph} (J cm^{-3})$^{1/2}$ [b]
d1	10.8	12.9
d2	11.0	7.2
d3	10.6	12.6
d4[c]	10.9	12.5

[a] Determined from plot of ΔT_g as a function of polymer δ_{ph} assuming that maximum T_g occurs when dye and polymer solubility parameters are equal

[b] Calculated from group contributions listed by Van Krevelen[20]

[c] Data illustrated in a previous publication[15]

All figures have the same appearance qualitatively. For low values of polymer δ_{ph}, ΔT_g is low. As δ_{ph} increases, ΔT_g rises, peaks at a maximum and then falls to a low value. The appearance of these data are very similar to the previous study on disazothiophene–polymer blends and qualitatively identical to the determination of polymer solubility parameters by swelling measurements in solvents of different solubility parameter[20,21]. The amount of solvent absorbed depends on the solubility parameter of the solvent with maximum swelling occurring when the solubility parameters of solvent and polymer are equal. Relating these results to the current study on dye–polymer affinity, since enhanced dye–polymer affinity would be expected to result in a higher T_g, the peak position should define the point at which the solubility parameters of the dye solute and
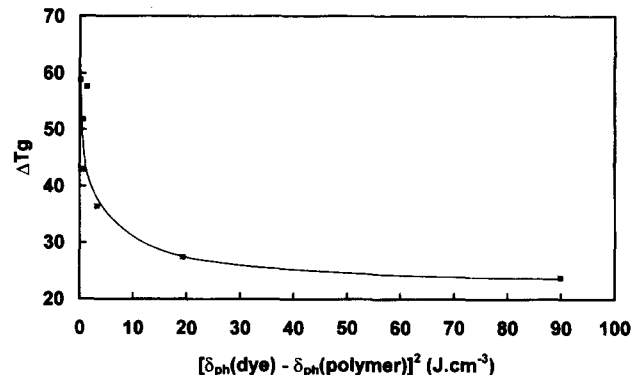

Figure 7 The variation of ΔT_g with dye–polymer solubility parameter difference for dye d2 blends
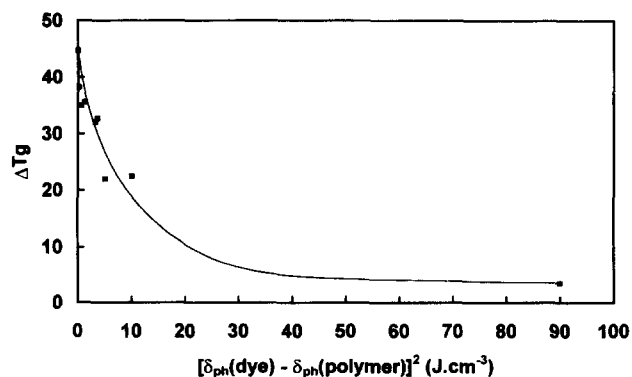

Figure 8 The variation of ΔT_g with dye–polymer solubility parameter difference for dye d3 blends

polymer matrix are equal. Essentially, this method is an experimental determination of solute solubility parameter. The dye δ_{ph} values determined in this fashion are compared to those calculated via group contributions in *Table 7*. The results suggest that the calculated solubility parameters are subject to error. This may not be surprising since the types of functional group listed[20] are limited with the result that non-aromatic ring closures and conjugated rings cannot be accounted for.

The relationships between ΔT_g and dye–polymer solubility parameter difference are illustrated in *Figures 6–8* for dyes d1, d2 and d3, respectively. The results agree with the previous study on disazothiophene in various polymers[15]. ΔT_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. The T_g is highest when the solubility parameters of dye and polymer approach equality. There are a few previous cases where plasticization phenomena have been related to solute–polymer affinity and solubility parameter differences between solutes and polymers. Investigating the effects of solute type on the plasticization of PET, Ingamells and Yanumet[22] 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[23] illustrated that there was a relationship between T_g and the difference in average polar and hydrogen bonding solubility parameters between PAN and the 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 these cases matching solubility parameters and solute–polymer affinity was found to increase plasticization and decrease the T_g which 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 semi-crystalline polymers, and the effects of plasticizer on the disruption of crystallinity was not studied. It is possible that solutes with a high affinity for the polymer could enhance the extent of amorphous polymer, producing different amounts of amorphous polymer accessible for plasticization. There are two other possible explanations for the plasticization effects. In the studies on PET and PAN the molecular weights of the solutes are low in comparison to our study on the dye solute. Alternatively, it is thought that the PET and PAN data are confused by the method used to perform 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 these polymers which are poor solvents will be low, and additionally they may not be molecularly dispersed and are likely to be aggregated because of the low solute–polymer affinity resulting 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[24,25]. 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 correctly elucidate 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 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[26] 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 a 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[1-6].

The results demonstrate that polar and hydrogen bonding interactions explain differences in the glass transition of solute–polymer blends, provided that dispersion forces (which are relatively short range) are ignored. However, polar and hydrogen bonding forces are longer range, and the results suggest that these longer range forces have more influence on the co-operative motions associated with the glass transition. The dye molecules have molecular weights which are three to five times that of a polymer repeating unit. From a mechanistic viewpoint, the dye–polymer blend can be thought of as a three-dimensional network in which the dye solutes can behave as physical crosslinks, co-operatively 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 increases the T_g. Including previously published data, this behaviour has been demonstrated for four fundamentally different dye structures in a variety of polymers, suggesting that this mechanism is general for relatively large solutes in polymers.

CONCLUSIONS

The effects of dye solute structures and polymer matrix structure on the T_gs of dye–polymer blends have been investigated. Three different solutes were investigated in a wide variety of polymers. The data were found to correlate well with a model where the T_g of the solute–polymer blend depends on the polymer T_g, the solute T_g, the relative concentration of solute and polymer, and the solute–polymer affinity.

Dye T_g was found to vary substantially. The dyes have widely differing effects as plasticizers with T_gs ranging from 70 to $-55°C$. The dye T_g followed the same order as dye melting point with the T_g/T_m ratio varying from 0.71 to 0.55 depending on structure.

In most cases, the experimentally determined T_g was higher than the T_g calculated using the Fox equation. This difference depended on the particular dye–polymer combination, and it was correlated with dye–polymer affinity using solubility parameters as a predictive tool. The use of global solubility parameters produced poor correlations. Averaging polar and hydrogen bonding solubility parameters produced excellent results, suggesting that these longer range forces are more important in controlling T_g. The

variation of T_g elevation with polymer solubility parameter only was found to be excellent producing a maximum T_g at a certain solubility parameter. The solubility parameter producing the maximum T_g was assumed to be the point of maximum dye–polymer affinity, to produce experimentally determined solubility parameters for the dyes. For all dyes, these values were different to those calculated from group contributions. The correlation between T_g and dye–polymer affinity (estimated via solubility parameter difference) was found to be very good in all cases. It was shown that the dye–polymer T_g was lowest with the greatest mismatch in dye–polymer affinity but increased as the dye–polymer compatibility increased resulting in the highest T_g when dye–polymer affinity was at a maximum. Similar trends were found for all solutes suggesting that the mechanism can be universally applied to relatively large solutes in polymers.

ACKNOWLEDGEMENTS

REFERENCES

1. Wessling, R. A., *Polyvinylidene Chloride*. Gordon and Breach, 1977.
2. Johnston, N. W., *J. Macromol. Sci., Chem.*, 1975, A9(3), 461.
3. Shih, J. S., Chuang, J. C. and Login, R. B., *Polym. Mater. Sci. Eng.*, 1992, 67, 266.
4. Vivas de Meftahi, M. and Frechet, J. M. J., *Polymer*, 1988, 29, 477.
5. Cowie, J. M. G., Garay, M. T., Lath, D. and McEwen, I. J., *Br. Polym. J.*, 1989, 21, 81.
6. Simmons, A. and Natahnson, A., *Macromolecules*, 1992, 25, 1272.
7. Simmons, A. and Natahnson, A., *Macromolecules*, 1991, 24, 3651.
8. Simmons, A. and Natahnson, A., *Macromolecules*, 1990, 23, 5127.
9. Fox, T. G., *Bull. Am. Phys. Soc.*, 1956, 1, 123.
10. Kelley, F. N. and Bueche, F., *J. Polym. Sci.*, 1961, 50, 549.
11. Couchman, P. R., *Macromolecules*, 1978, 11, 1156.
12. Gordon, M. and Taylor, J. S., *J. Appl. Chem.*, 1952, 2, 493.
13. Kwei, T. K., *J. Polym. Sci., Polym. Letts. Edn*, 1984, 22, 307.
14. Painter, P. C., Graf, J. F. and Coleman, M. M., *Macromolecules*, 1991, 24, 5630.
15. Slark, A. T., *Polymer*, in press.
16. Turi, E., *Thermal Characteristation of Polymeric Materials*. Academic Press, 1981.
17. Hansen, C. M., *J. Paint Technol.*, 1967, 39, 104, 511.
18. Hansen, C. M., *Ind. Eng. Chem. Prod. Res. Dev.*, 1969, 8, 2.
19. Barton, A., *Handbook of Solubility Parameters and other Cohesion Parameters*. CRC Press, FL, USA, 1983.
20. Van Krevelen, D. W., *Properties of Polymers*. Elsevier Science, New York, 1986.
21. Kern Sears, J. and Darby, J. R., *The Technology of Plasticisers*, John Wiley, New York, 1982.
22. Ingamells, W. and Yanumet, M., *Br. Polym. J.*, 1980, 12(1), 12.
23. Ingamells, W., *Solvents–Neglected Parameter, Solvent Symp.*, ed. G. Kakabadse. UMIST, Manchester, UK, 1977.
24. Sakelllariou, P., Rowe, R. C. and White, E. F. T., *Int. J. Pharm.*, 1986, 31, 55.
25. Sakellariou, P., Rowe, R. C. and White, E. F. T., *J. Appl. Polym. Sci.*, 1987, 34, 2507.
26. Kanig, G., *Kolloid Z.*, 1963, 190(1), 1.