

Polymers for Electronic Imaging: The Control of Dye Transport via Dye-Polymer Interactions

*A. A. Clifton, A. T. Slark and A. Butters
ICI Imagedata, Brantham, Manningtree, Essex, England*

Abstract

The transport of different dye solute molecules from various dye-donor polymer films to a constant dye-acceptor polymer film has been investigated. At constant dye concentration, the transport of all dye molecules from the dye-donor was found to be controlled by the T_g of the dye-polymer mixture. The data was found to fit well with free volume considerations. Further investigations were accomplished to understand the parameters influencing the key factor of dye-polymer blend T_g . This was found to depend on the polymer T_g , the dye solute T_g , their relative concentrations and dye-polymer affinity. Attempts were made to correlate increases in T_g with dye-polymer affinity using solubility parameters as a predictive tool and excellent correlations were established. The T_g was low when there was a large mismatch in solubility parameters, increased as dye and polymer became more compatible and reached a maximum when the solubility parameters of both components were equal. The results demonstrate the need for complementary dye and polymer materials design.

Introduction

Thermal transfer printing is a method for producing high quality continuous tone colour images from an electronic source. The printing process involves the transfer of dye from a donor ribbon to an acceptor sheet when the two are brought into intimate contact at high temperature and pressure¹. The temperature of dye transfer and the print time can vary but maximum values are typically 250 °C and 10 milliseconds, 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.

Typically, both the donor ribbon and acceptor sheet for thermal transfer printing are multilayer structures with each layer performing a particular function. 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 sublimation².

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. In the present work a lower temperature dye transfer method has been employed to elucidate the most important structural factors controlling the release of dye from the donor matrices.

It is the purpose of this paper to report on the influence of dye-polymer interactions in a donor polymer matrix on dye transport, where the dye solute concentration is high. The information disclosed is, however, relevant to the general behaviour of organic solutes in polymers.

2. Method

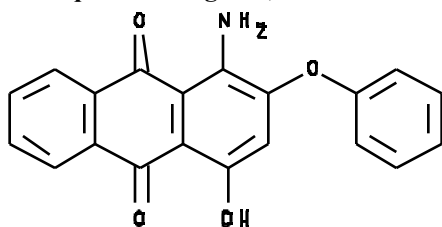
Film Preparation and Drying

The dyes and polymers used are listed in Figure 1 and Table 1, respectively. Dyes were used as supplied by Zeneca Specialities and polymers were used as obtained from the various suppliers listed in Table 1. Dyes and polymers were dissolved in tetrahydrofuran (THF) solvent according to the following mixtures (all %-w/w):

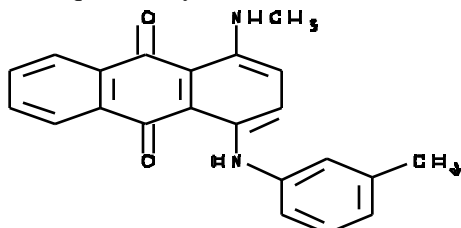
- d1 anthraquinone magenta dye 6% / polymer 3% / THF 91.0%
- d2 anthraquinone cyan dye 4.5% / polymer 4.5% / THF 91.0%
- d3 isothiazole magenta dye 3.0% / polymer 6.0% / THF 91.0%
- d4 disazothiophene cyan dye 2.25% / polymer 4.50% / THF 93.25%

The formulations were coated on to polyester substrates using wire bars. Coatings were dried under various conditions and analysed by Head Space Gas Chromatography using a Perkin-Elmer Sigma 2000 Gas Chromatograph to determine the quantity of residual tetrahydrofuran. It was found that post-heating the coated film for 30 seconds at 110°C was necessary for effective solvent removal (THF < 0.05 $\mu\text{g}\cdot\text{cm}^{-2}$). All films were assessed using optical microscopy prior to evaluation, to check that no undissolved dye particles or crystals were present.

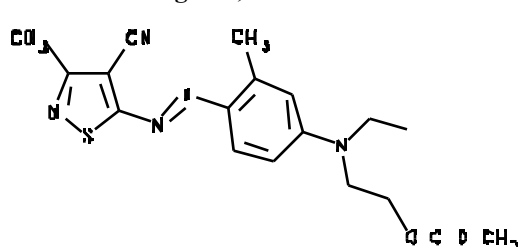
anthraquinone magenta, d1



anthraquinone cyan, d2



isothiazole magenta, d3



disazothiophene cyan, d4

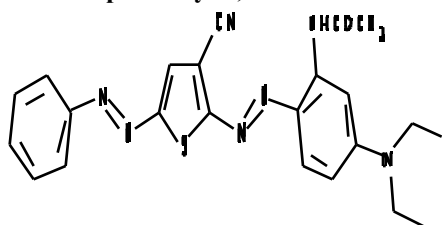


Figure 1 Structures of dye molecules studied.

Dye diffusion studies

Dye-polymer donor films were prepared on 6 μm polyester base (obtained from *Diafoil*) as described previously. These films were then placed in contact with an acceptor medium which was kept constant throughout the experiments. The acceptor layer was a 4 μm coating of a copolyester, "Vylon 103" (obtained from Toyobo) having a T_g of 47 $^{\circ}\text{C}$. The acceptor polymer was coated onto a thick opaque polyester substrate ("Melinex 990" from ICI Films). The dye was transferred from the donor film to the acceptor film using an Ozatec HRL350 2-roll laminator with thermostatically controlled rollers. The donor and acceptor films were placed in intimate contact and fed through the laminator. The temperature of the laminator was constant at 65 $^{\circ}\text{C}$ with a nip pressure of 5 bar and a roll speed of 0.2 metres/minute. Therefore, the transfer temperature (65 $^{\circ}\text{C}$) is always above the T_g of the acceptor polymer matrix (47 $^{\circ}\text{C}$). After transfer, the polymer films were separated and the

amount of dye transferred was assessed via optical density measurements using a Sakura PDA-65 optical densitometer. The reflection optical density of the non-dyed acceptor film was subtracted to measure the absolute amount of dye transfer.

Table 1. Properties of polymers used in donor matrices.

polymer type	supplier	T_g ($^{\circ}\text{C}$)
cellulose acetate	Eastman	
butyrate	Chemical	93.0
ethyl cellulose	Hercules	
		93.0
polystyrene	Polysciences	
		104.5
poly(styrene-co-acrylonitrile)	Polysciences	
		103.0
poly(p-hydroxy styrene)	Maruzen	
	Petrochemical	145.0
polyester	Dynamit	
	Nobel	100.0
polycarbonate	Dow Chemical	
		100.0
poly(vinyl chloride)	Polysciences	
		82.5
chlorinated	Zeneca Resins	
poly(vinyl chloride)		99.0
poly(vinyl butyral)	Sekisui	
		85.0
poly(vinyl aceto acetal)	Sekisui	
		96.0
poly(vinyl formal)	Monsanto	
		86.5
phenoxy	Union Carbide	
		78.5

Determination of T_g of dye-polymer blend coatings

A Perkin-Elmer DSC-4 instrument, calibrated with an Indium standard, was used to determine all thermal transitions at a heating rate of 20 $^{\circ}\text{C}/\text{minute}$. For the polymers, T_g values were determined in the standard fashion from second runs on solid samples but for dye-polymer blends T_g measurements were made during the first heating cycle. Dye-donor polymer mixtures were applied from tetrahydrofuran onto uncoated 3.5 μm polyester base to a thickness of approximately 3 μm and dried for 30 seconds at 110 $^{\circ}\text{C}$. 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.

3. Results

The effect of dye-polymer T_g on transport

Figures 2, 3, 4 and 5 represent the optical density data as a function of the dye-polymer blend T_g in the donor

matrix for dyes d1, d2, d3 and d4, respectively. The data clearly shows that the glass transition of the dye-polymer blend has a controlling influence on dye diffusion. Figures 2-4 demonstrate that there is a strong inverse relationship between dye diffusion and the initial T_g of the dye-polymer donor matrix, at constant transfer temperature (correlation coefficients 0.94, 0.90 and 0.81, respectively). It is important to recognise that this relationship is applicable to these systems, independent of both the dye and polymer structure in the donor matrix. Conversely, the diffusion of dye d4 (Figure 5) appears to be independent of the dye-polymer T_g in the donor matrix, giving very low levels of transfer in all cases. This apparent difference is a direct consequence of the variation in absolute values of dye-polymer T_g for a particular dye-donor matrix. The range of dye-polymer blend T_g values varies substantially for the same group of polymers. The relative magnitudes of dye-polymer blend T_g for the various donor matrices ranged from 42-67 °C, 38-80 °C, 27-55 °C and 83-120 °C for d1-d4 respectively. The key to transfer under these conditions is the relative magnitude of dye-polymer T_g to the temperature of transfer, 65 °C. For those dyes (d1, d2 and d3) where the majority of dye-polymer T_g values are less than 65 °C-70°C, significant dye transfer occurred with the interval, T-T_g, being an important factor in controlling the amount of transport. However, for d4, the transport was consistently very low since the dye-polymer T_g was always significantly greater than the transfer temperature.

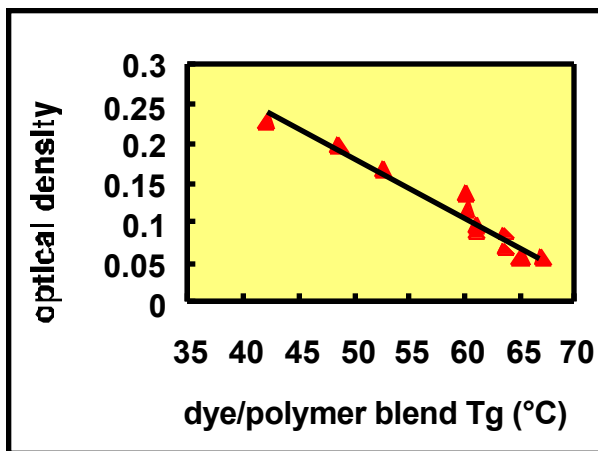


Figure 2: Transport of dye d1 from various dye-donors to polyester

Factors affecting T_g

The solute-polymer T_g values obtained have been used to test the model illustrated in Figure 6.

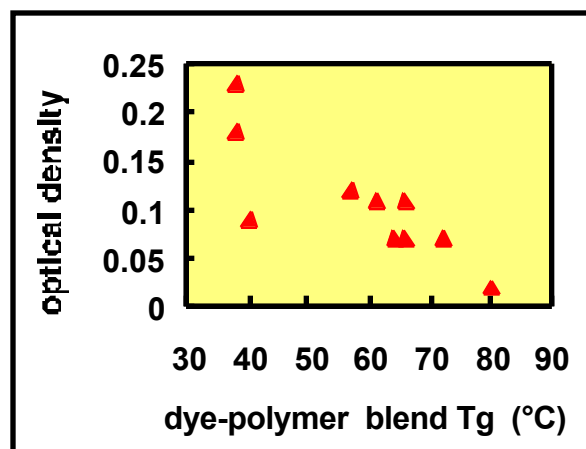


Figure 3: Transport of dye d2 from various dye-donors to polyester

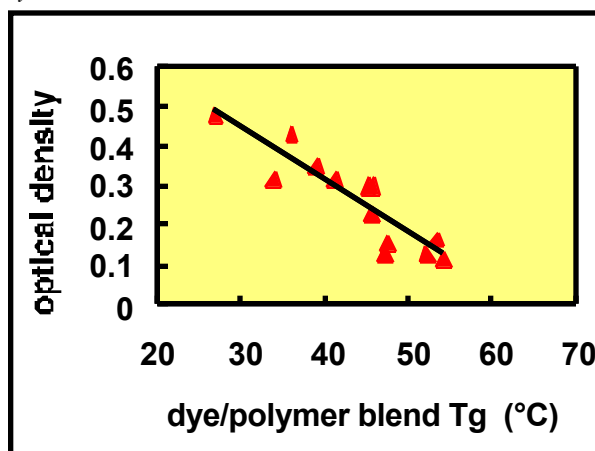


Figure 4: Transport of dye d3 from various dye-donors to polyester

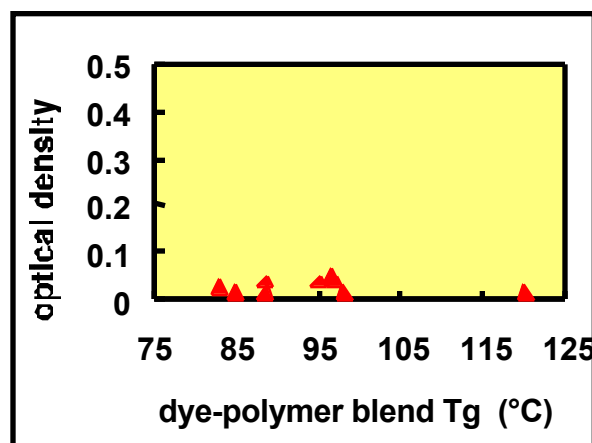


Figure 5: Transport of dye d4 from various dye-donors to polyester

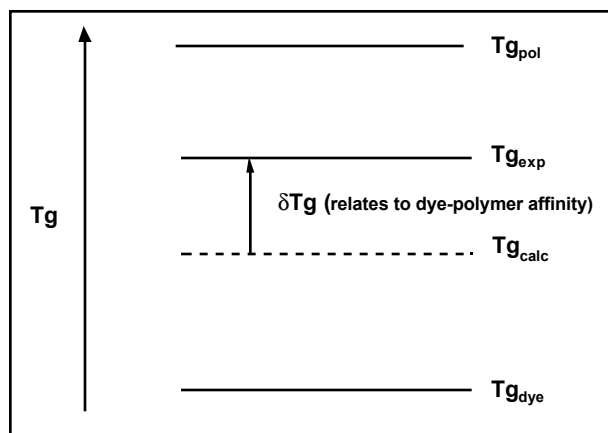


Figure 6: Overall model of factors influencing the T_g of solute-polymer blends.

In this model, the actual solute-polymer T_g depends on the polymer T_g ($T_{g_{pol}}$ defined by its structural characteristics), the solute T_g ($T_{g_{dye}}$ 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 described by the Fox equation [3]:

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

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-ethyl cellulose (EC) combination as a reference point. It was assumed that the dye-EC combination most nearly obeyed the Fox relationship, allowing calculation of the dye T_g ($T_{g_{dye}}$) from measurement of the blend T_g ($T_{g_{exp}}$) and polymer T_g using equation 1. Then using this dye T_g , $T_{g_{calc}}$ was determined for the other polymers using equation 1. It should be noted that the experimental T_g was generally higher than the calculated T_g . This difference was then correlated with the dye-polymer affinity using the parameters, δT_g and ΔT_g which are defined below in equations 2 and 3.

$$\delta T_g = T_{g_{exp}} - T_{g_{calc}} \quad (2)$$

$$\Delta T_g = \frac{(T_{g_{exp}} - T_{g_{calc}})}{(T_{g_{pol}} - T_{g_{calc}})} \times 100 \quad (3)$$

The variation of dye solute T_g

The calculated T_g values for the various dyes are shown in Table 2 and compared to the actual melting points of

crystalline dye. The data suggests that the dyes will have widely differing effects as plasticisers with their T_g 's ranging from 70 °C to -55 °C. Dye d3 is an excellent plasticiser since its T_g is very low whereas dye d4 is a poor plasticiser. For certain dye-polymer combinations, dye d4 actually causes antiplasticisation 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 $T_g = BT_m^4$. The accuracy of the dye T_g predicted from the dye-EC reference point was investigated using DSC. Crystalline dye d4 was heated above its melting point to 225 °C and supercooled to room temperature at a rate of 200 °C per minute. A second run of the sample was then taken and a glass transition for the dye was observed at 68 °C. This T_g is very similar to the T_g of 70 °C predicted from the dye-EC combination using the Fox equation, thereby vindicating the previous assumptions.

Table 2. Thermal properties of dyes

dye	$T_{g_{dye}}$ (°C)	T_m (°C)	T_g (K) / T_m (K)
d3	-55	120	0.56
d2	-3	127	0.68
d1	17	185	0.63
d4	70	210	0.71

The effect of intermolecular forces on T_g

We have attempted to correlate enhancement in T_g with dye-polymer interaction using solubility parameters as a guide to dye-polymer affinity. Separate component solubility parameters were calculated via the method according to Hansen⁵ and the averaged polar/hydrogen bonding parameter (δ_{ph}) was found to give the best fit to the data. The relationships between ΔT_g and polymer δ_{ph} are illustrated in Figures 7, 8, 9 and 10 for the dye-polymer blends of dyes d1, d2, d3 and d4, respectively. 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 this data is qualitatively identical to the determination of polymer solubility parameters by swelling measurements in solvents of different solubility parameter^{4,6}. 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 higher T_g , the peak position should define the point at which the solubility parameters of the dye solute and polymer matrix are equal. Essentially, this method could be viewed as 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 3. The results suggest that the calculated solubility parameters are subject to error. This may not be surprising since the types of functional group listed⁴ are limited with the result that non-aromatic ring closures and conjugated rings cannot be accounted for.

Table 3. Comparison of experimental and calculated solubility parameters.

dye	experimental $\delta_{ph} (\text{J.cm}^{-3})^1$	calculated $\delta_{ph} (\text{J.cm}^{-3})^1$
d1	10.8	12.9
d2	10.6	7.2
d3	10.6	12.6
d4	10.9	12.5

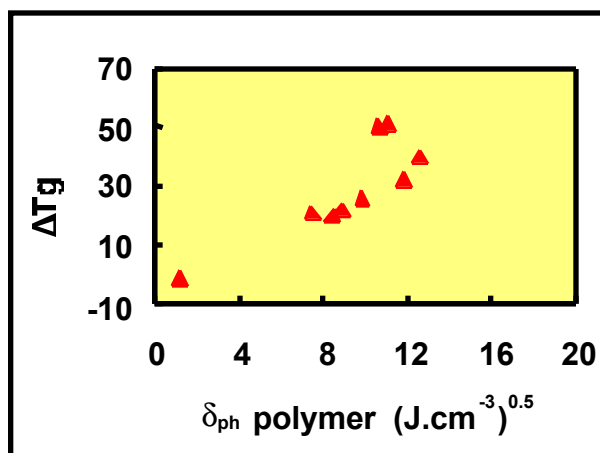


Figure 7: Variation in Tg enhancement with polymer solubility parameter for dye d1.

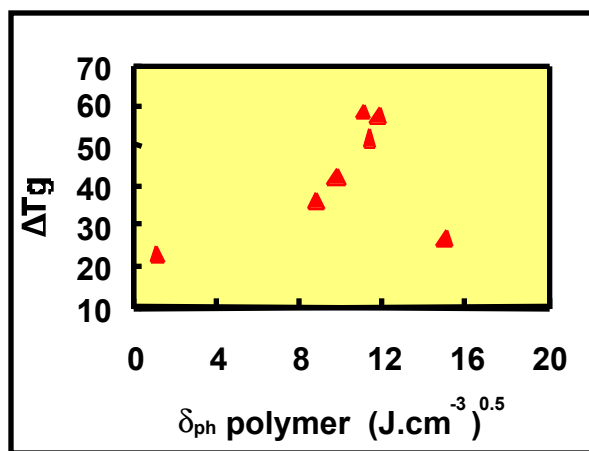


Figure 8: Variation in Tg enhancement with polymer solubility parameter for dye d2.

The results suggest that ΔT_g is low when there is a large difference in dye-polymer affinity but the elevation in Tg increases as dye-polymer affinity is enhanced. The Tg is highest when the solubility parameters of dye and polymer approach equality. Our results agree with the work of Kanig⁷

on mixtures of polymer and plasticiser. He predicted that a good plasticiser is a poor solvent and that low affinity plasticisation and low Tg. Conversely, a poor plasticiser is a good solvent and high affinity between plasticiser and polymer results in higher Tg. Our results also agree with those of previous workers for copolymers or polymer blends where interactions lead to increases in Tg⁸⁻¹³. From a mechanistic viewpoint, the dye-polymer blend can be considered to be a 3-dimensional network in which the dye solutes can behave as physical crosslinks. The size of the dye solutes is 2-4 times that of a typical polymer repeating unit. It is expected that the dyes could interact co-operatively 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 Tg.

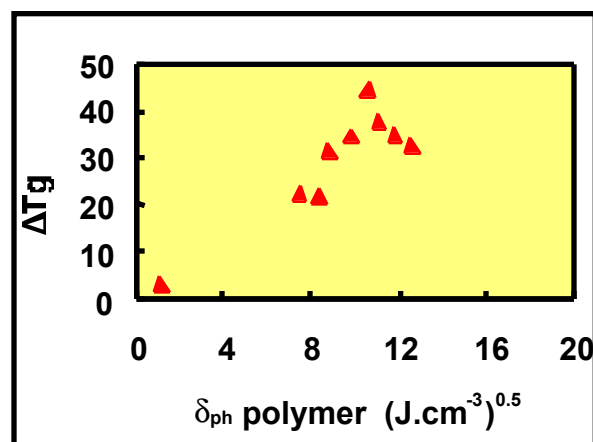


Figure 9: Variation in Tg enhancement with polymer solubility parameter for dye d3.

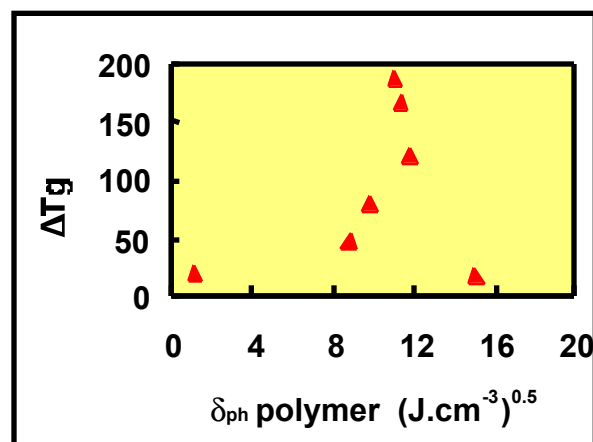


Figure 10: Variation in Tg enhancement with polymer solubility parameter for dye d4.

4. Conclusions

(1) At constant ratio of dye solute to dye-donor polymer, the rate of dye transport from a polymeric donor matrix is controlled by the glass transition of the dye-polymer blend.

(2) For systems where the dye-polymer T_g values are lower than the transfer temperature, the amount of dye transported at constant temperature to a fixed acceptor polymer is inversely proportional to the T_g of the dye-polymer mixture in the donor matrix. This relationship is independent of both dye and polymer chemical composition for the materials studied.

(3) The glass transition of the dye-polymer blend depends on the polymer T_g, the dye T_g, the relative dye/polymer concentrations and the dye-polymer interaction. Dye T_g was found to vary substantially. The dyes have widely differing effects as plasticisers with T_g's ranging from 70 °C 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.

(4) In all cases, the actual T_g was higher than the calculated 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 defined solubility parameter. This maximum was assumed to be the point of optimum dye-polymer affinity where dye and polymer solubility parameters were equal. This value was different to that calculated for the dye from group

contributions, suggesting that the latter is subject to error. (5) 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 dye-polymer affinity enhanced, resulting in the highest T_g when the dye-polymer affinity was at a maximum.

5. References

- [1] Hann, R.A. and Beck, N.C., *J. Imaging Technology*, **16**, 238, (1990).
- [2] Hann, R.A., unpublished results.
- [3] Fox, T.G. *Bull. Am. Phys. Soc.*, **1**, 123, (1956).
- [4] Van Krevelen, D.W. "*Properties of Polymers*", Elsevier Science, 1986.
- [5] Hansen, C.M., *J. Paint Technol.*, **39**, 104 and 511, (1967); *ibid.*, *Ind. Eng. Chem. Prod. Res. Dev.*, **8**, 2, (1969).
- [6] Kern Sears, J. and Darby, J.R. "*The Technology of Plasticisers*", John Wiley and Sons, New York, 1982.
- [7] Kanig, G. *Kolloid Z.*, **190**(1), 1, (1963).
- [8] Wessling, R.A. "*Polyvinylidene Chloride*", Gordon and Breach, 1977.
- [9] Johnston, N.W. *J. Macromol. Sci.; Chem.*, **A9**(3), 461, (1975).
- [10] Shih, J.S., Chuang, J.C. and Login, R.B. *Polym. Mater. Sci. Eng.*, **67**, 266, (1992).
- [11] Vivas de Meftahi, M. and Frechet, J.M.J. *Polymer*, **29**, 477, (1988).
- [12] Cowie, J.M.G., Garay, M.T., Lath, D. and McEwen, I.J. *Br. Polym. J.*, **21**, 81, (1989).
- [13] Simmons, A. and Natahnson, A. *Macromolecules*, **25**, 1272, (1992).