# Controlling dye delivery in electronic imaging via dye-polymer interactions

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# Agenda

1. Introduction to D2T2
2. Dye-polymer interactions in the donor layer
3. Dye-polymer interactions in the acceptor layer
4. Dye-dye interactions…
5. Conclusions



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# Dye Diffusion Thermal Transfer (D2T2) Printing

- Photo realistic images -  continuous tone printing process
- High resolution, 20 OD levels per colour – 8 million colours
- High print speeds – 6 x 4 inch photo printed in 5 seconds

- Major Applications
  - ✓ Digital photo finishing – Photobooths, Kiosks
  - ✓ Novelty photo – Events and Rides
  - ✓ ID Card personalisation – National ID Cards, Driving Licences, Credit Cards

# ITW Imagedata - D2T2 Product Assembly for ID Cards

**YMC Dye panels**

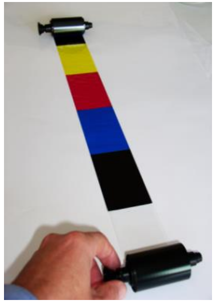
2 dyes + PVB/EC binder

Diffusion of dye into card

release from card

control of delivery rate of dye

have to compensate for back diffusion

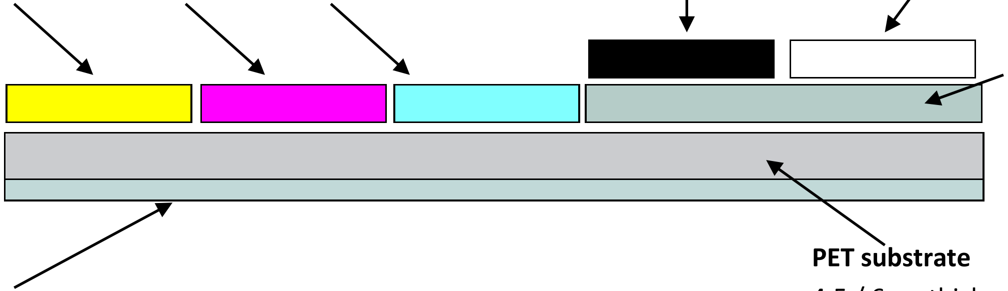


- **K Panel** - IR readable text & barcodes

Carbon black + resins

**Overlay** - image protection

Polyester resin



**Sub coat** - release of K & Overlay

UV Cured acrylic

**Back coat**

UV cured acrylic

solid lubricant

lubricates passage of thermal head over media

must not corrode ceramic on the head

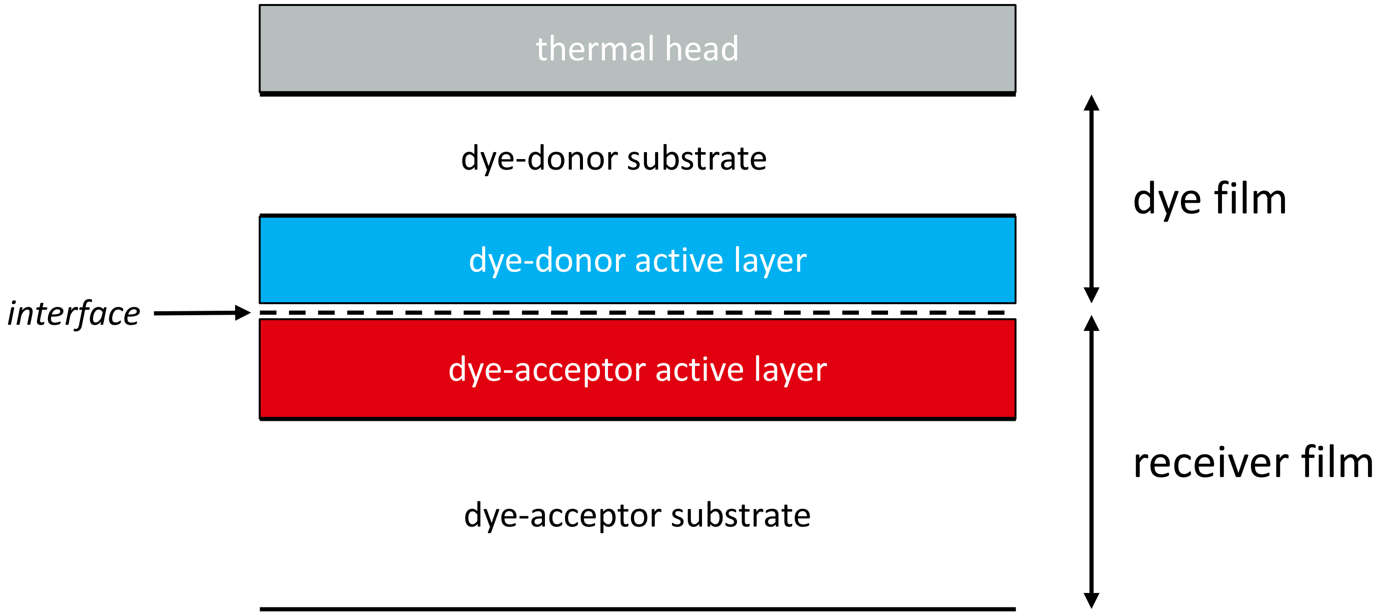
**PET substrate**

4.5 / 6um thick

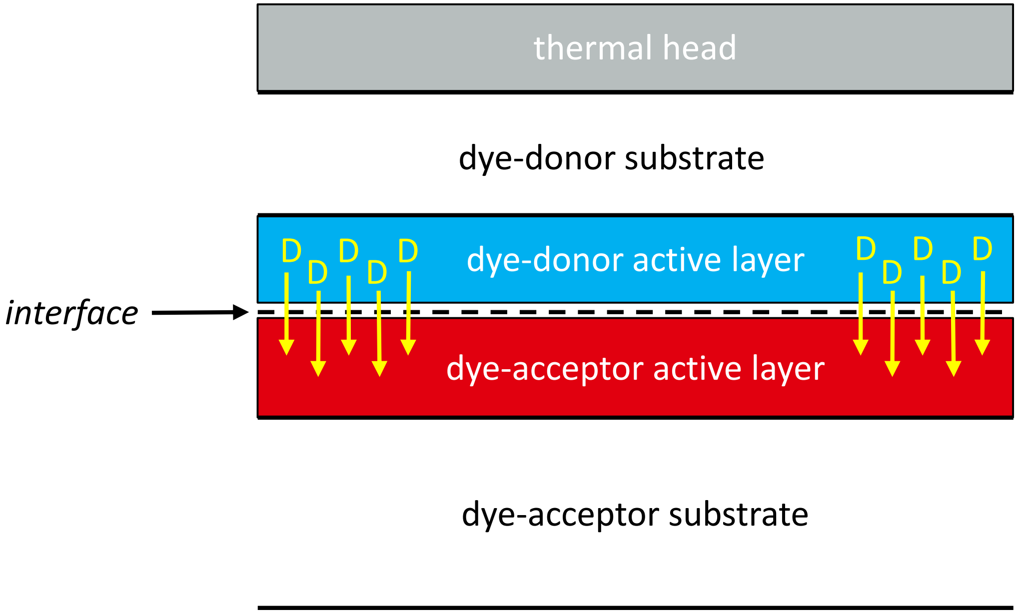
adhesion pre-treated

pre-tensilised

# Dyes transfer via diffusion from donor to acceptor layers



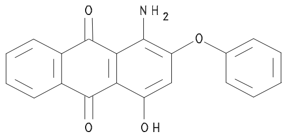
# Dyes transfer via diffusion from donor to acceptor layers

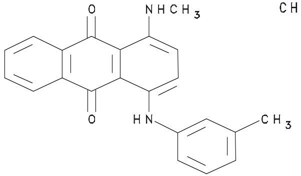


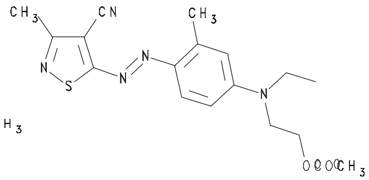

- dyes transfer by diffusion not sublimation
- temperature cycle 150 – 300 $^{0}$C for milliseconds
- constant print time = fixed temperature cycle

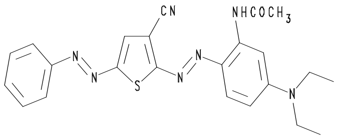
**Important to control dye transfer for colour density and colour balance**

# Dye-donor systems





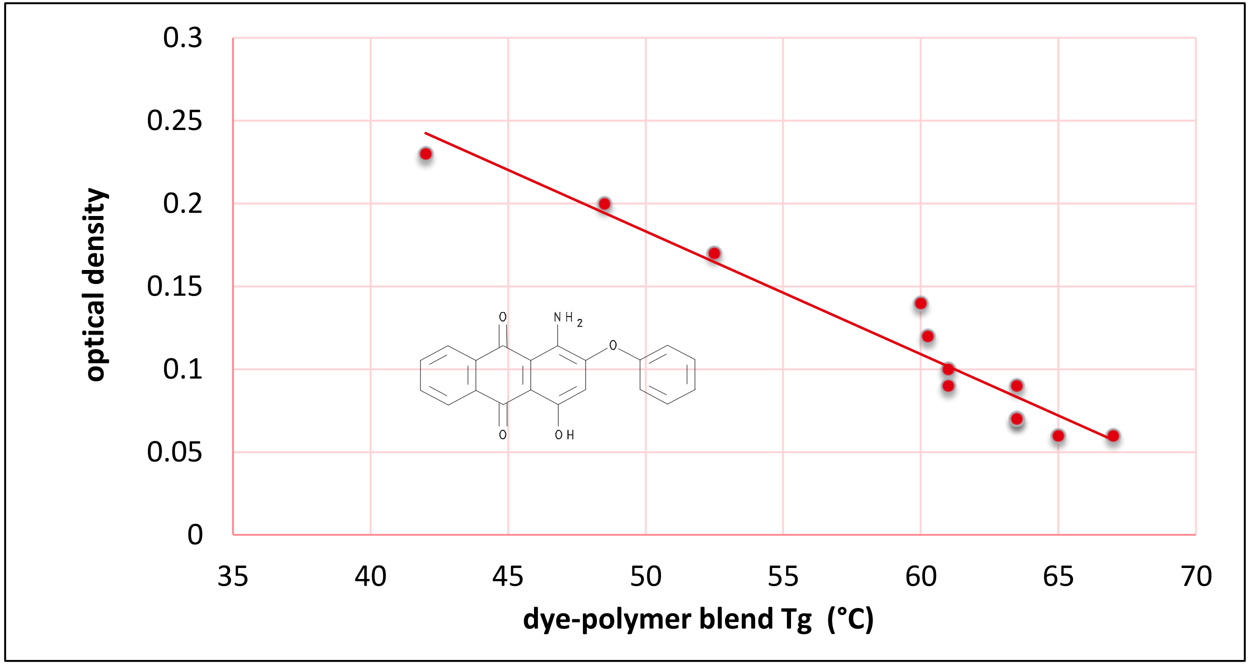




| polymer | Tg (°C) | d1-donor Tg (°C) | d2-donor Tg (°C) | d3-donor Tg (°C) | d4-donor Tg (°C) |
|---|---|---|---|---|---|
| CAB | 93.0 | 42.0 | ------ | ------ | ------ |
| EC | 93.0 | 48.5 | 38.0 | 26.5 | 85.0 |
| PS | 104.5 | 52.5 | 57.0 | 34.0 | 95.0 |
| PVC | 82.5 | 60.0 | ------ | 41.5 | ------ |
| PC | 100.0 | 61.5 | ------ | 45.5 | ------ |
| PEST | 100.0 | 61.0 | ------ | 45.0 | ------ |
| PHEN | 78.5 | 61.0 | ------ | 46.0 | ------ |
| CPVC | 99.0 | 63.5 | 65.5 | 53.0 | 97.0 |
| PVB | 85.0 | ----- | 61.0 | 39.0 | 89.0 |
| SAN | 103.0 | 63.5 | 64.0 | 54.0 | 97.0 |
| PVAA | 96.0 | 65.0 | 72.0 | 52.0 | 98.0 |
| PVF | 86.5 | 67.0 | 65.5 | 47.5 | 91.0 |
| PPHS | 145.0 | ----- | 80.0 | ------ | 120.0 |

increasing polarity

# | Dye transfer controlled by Tg of dye-polymer blend




Similar behaviour observed for other dyes



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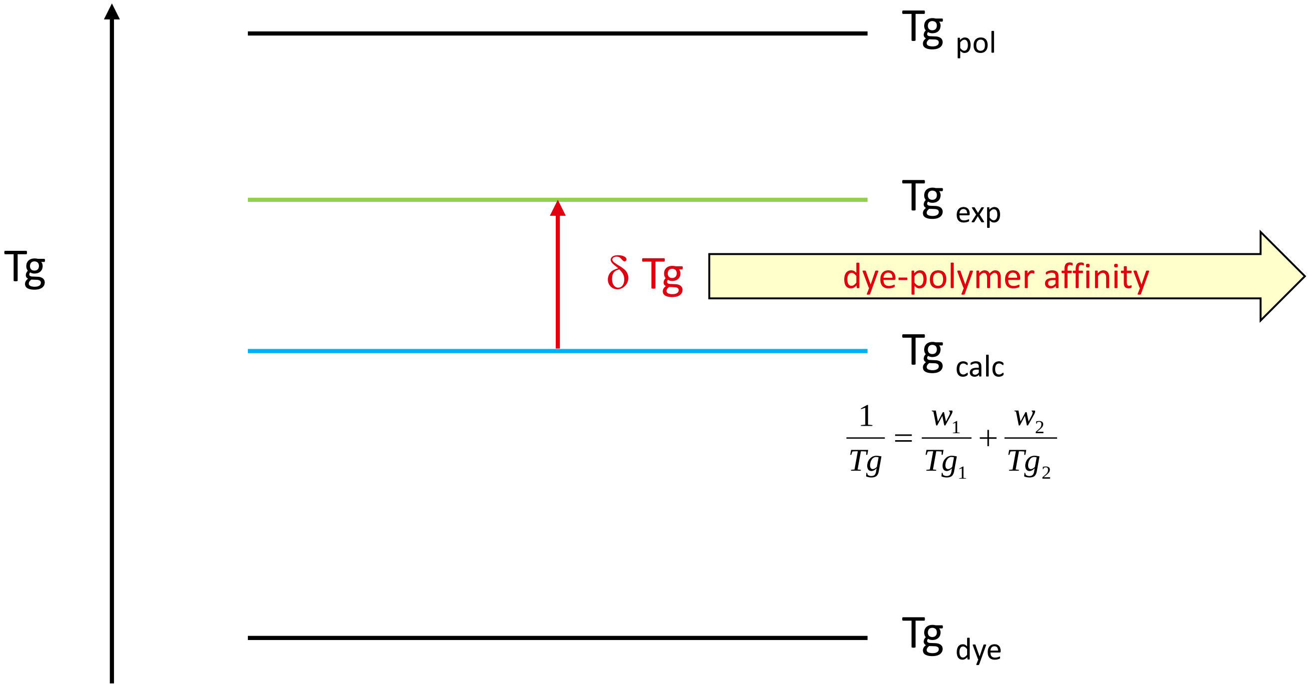
# Model of factors influencing Tg



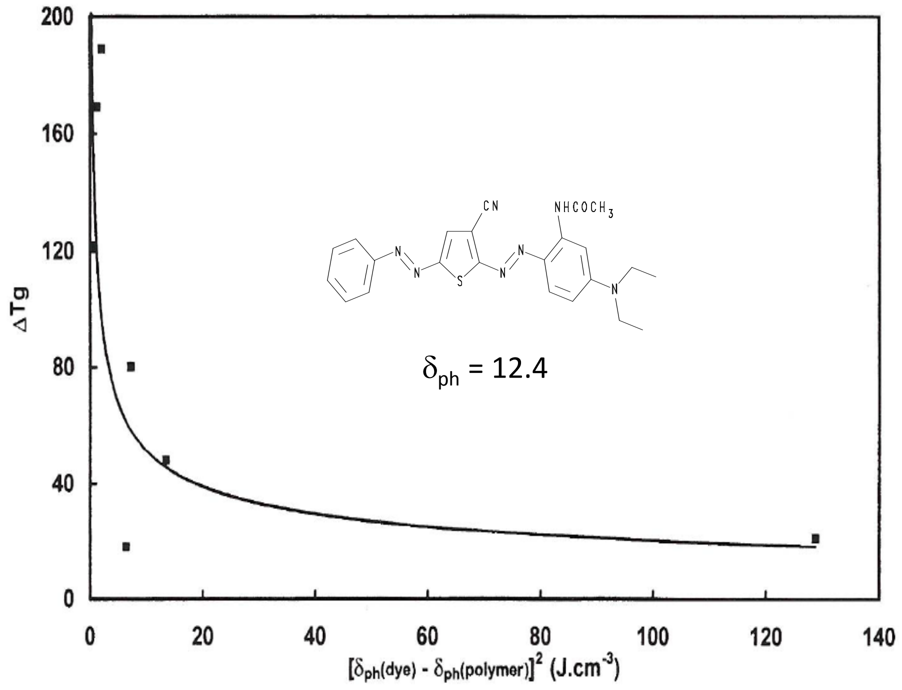

$$\frac{1}{Tg} = \frac{w_1}{Tg_1} + \frac{w_2}{Tg_2}$$

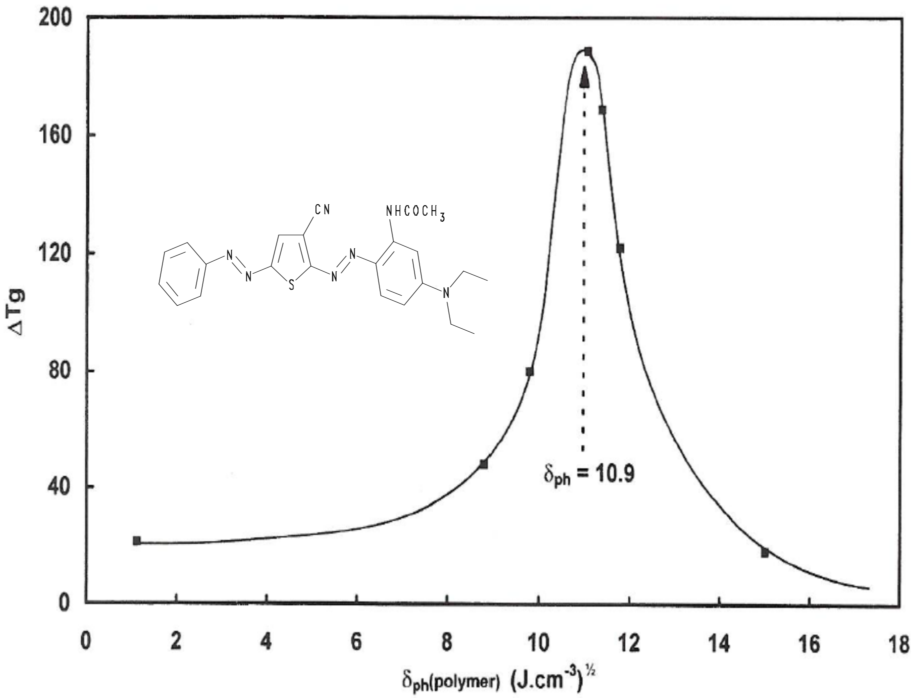
$$\delta_{ph}^2 = \delta_p^2 + \delta_h^2$$

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

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

# Higher Tg from stronger dye-polymer interactions




Similar behaviour observed for other dyes



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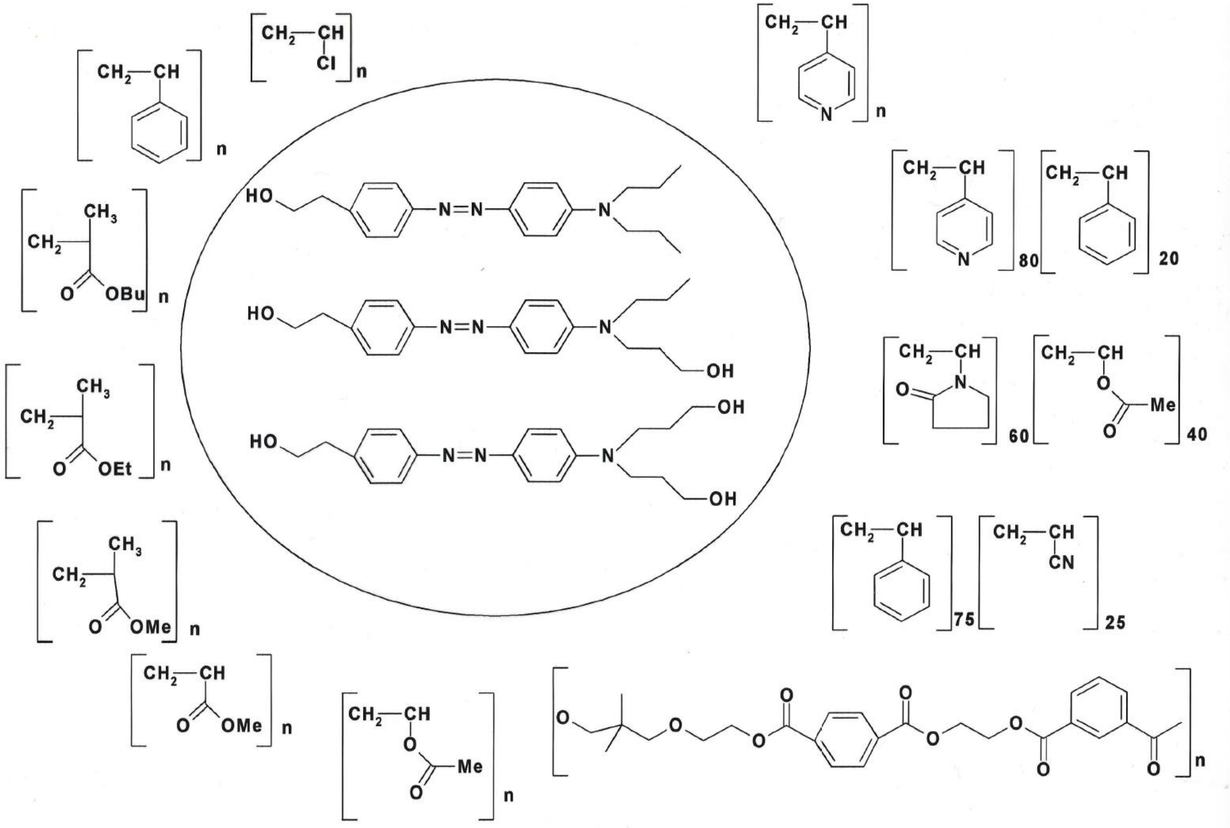
# Dye-acceptor systems



# Development of Solution-Diffusion Model

Permeability = Diffusivity x Solubility

$$P = D.S$$

diffusion coefficient relates to free volume

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

free volume depends on difference between transport temperature and Tg

$$f = f_g + \alpha\left(T - T_g\right)$$

solubility coefficient relates to heat of solution

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

$$\Delta H = \Delta H_{physical} + \Delta H_{specific}$$

endothermic:
solubility parameter difference

$$\Delta H_{physical} = \phi_d \phi_p \left(\delta_d - \delta_p\right)^2$$

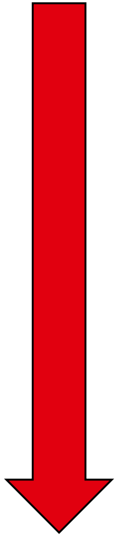
exothermic:
specific interactions

$$\Delta H_{specific} = function\left(\nu_{inter} - \nu_{free}\right)$$

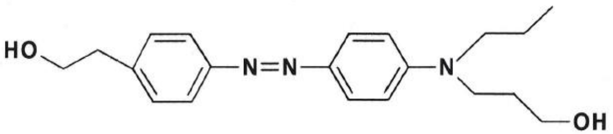
$$\ln P = a_4 + b_4\left(\frac{1}{Tg}\right) - c_4\left(\delta_d - \delta_p\right)^2 - d_4\left(\nu_{inter} - \nu_{free}\right)$$

# Bihydroxyl dye transfer to different acceptor polymers

| polymer | functional group | Tg (°C) | O-H- - X ($cm^{-1}$) |
|---|---|---|---|
| PVC | -Cl | 88.0 | 3602 |
| PS | -phenyl | 110.8 | 3583 |
| PBMA | -COO- | 71.5 | 3544 |
| PES1 | -COO- | 47.0 | 3547 |
| PES2 | -COO- | 69.0 | 3547 |
| PMMA | -COO- | 122.0 | 3541 |
| PEMA | -COO- | 80.0 | 3541 |
| PMA | -COO- | 19.5 | 3541 |
| PVAc | -COO- | 41.7 | 3520 |
| P(S-co-AN) | -CN, -phenyl | 110.3 | 3518 |
| P(VPy-co-VAc) | -CON-, -COO- | 61.6 | 3368 |
| P(VP-co-S) | -N=, phenyl | 97.0 | 3281 |
| PVP | -N= | 90.0 | 3279 |



increasing specific interaction



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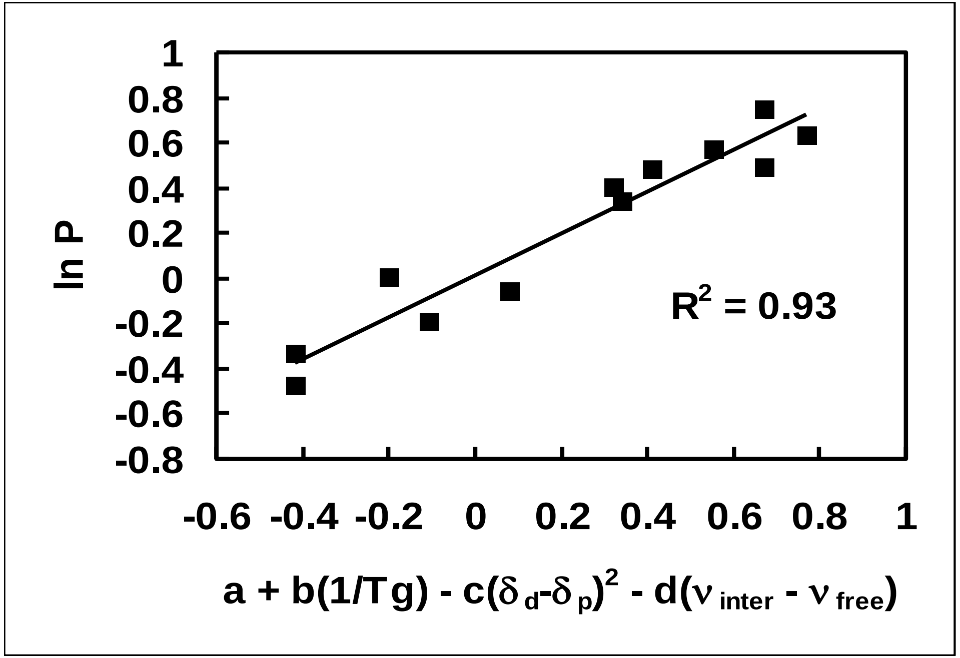
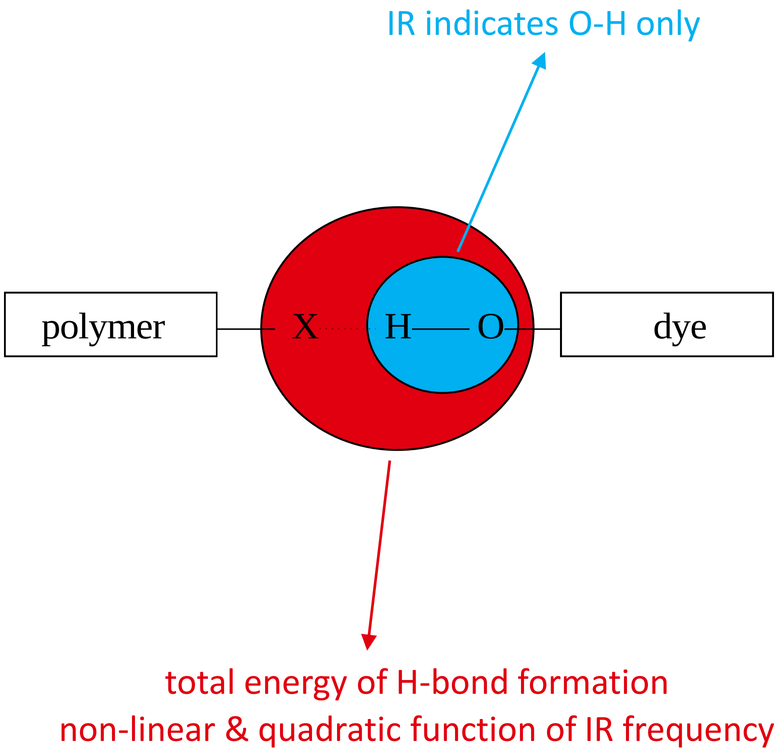
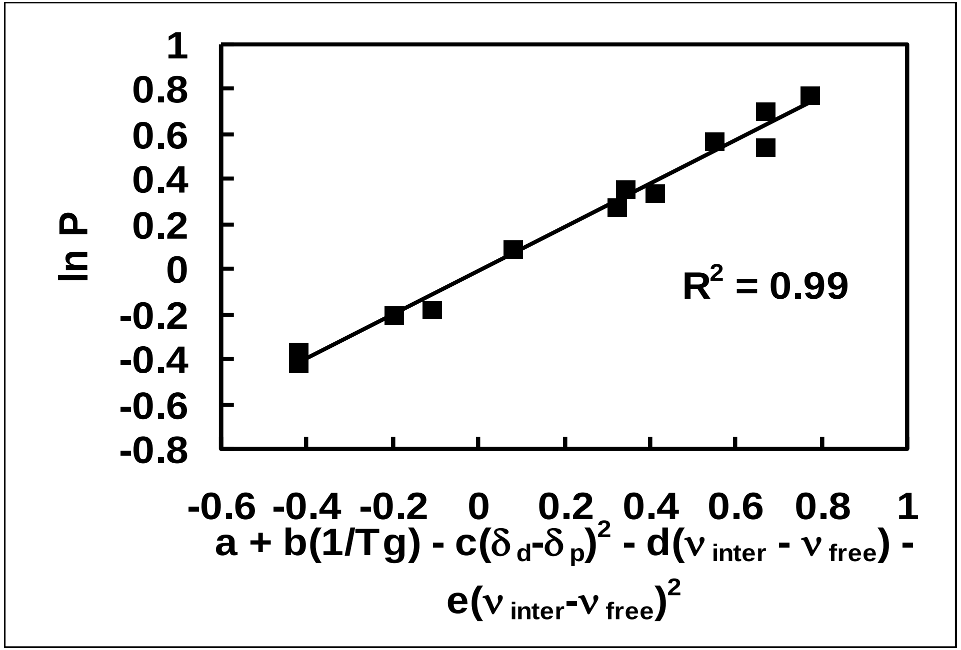


# Bihydroxyl dye transfer to different acceptor polymers



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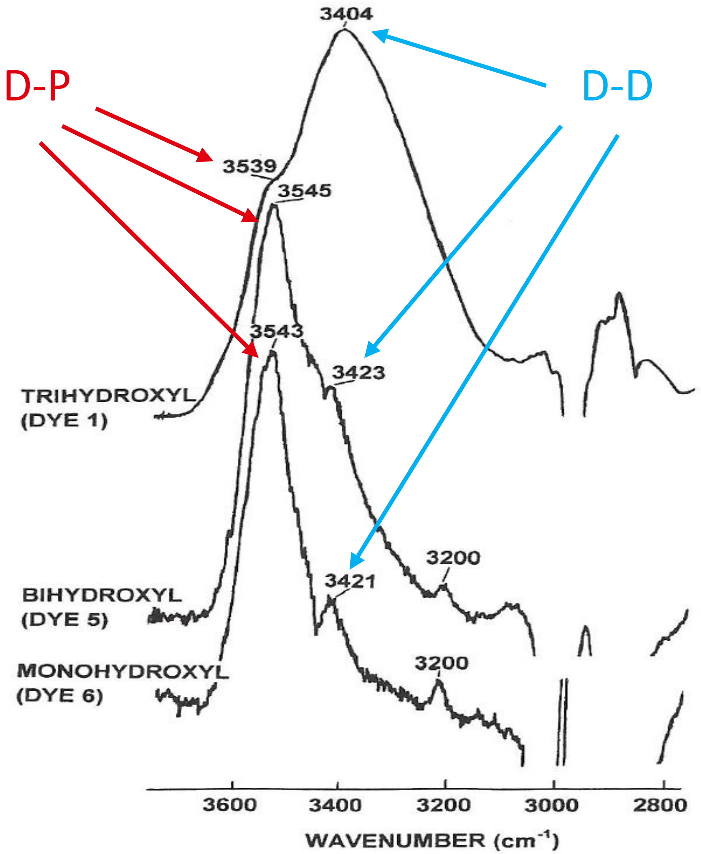
# Dye-dye interactions…………..dye-polymer interactions

various dyes: fixed polyester




D-P interaction strength

- similar for different dyes

D-D interaction strength

- D-D always stronger than D-P
- hydroxyl F3 > (F2 ~ F1)

D-D: D-P ratio

- hydroxyl F3 >> F2 > F1



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# Dye-dye interactions…………..dye-polymer interactions

fixed dye: various polymers

D-P interaction strength

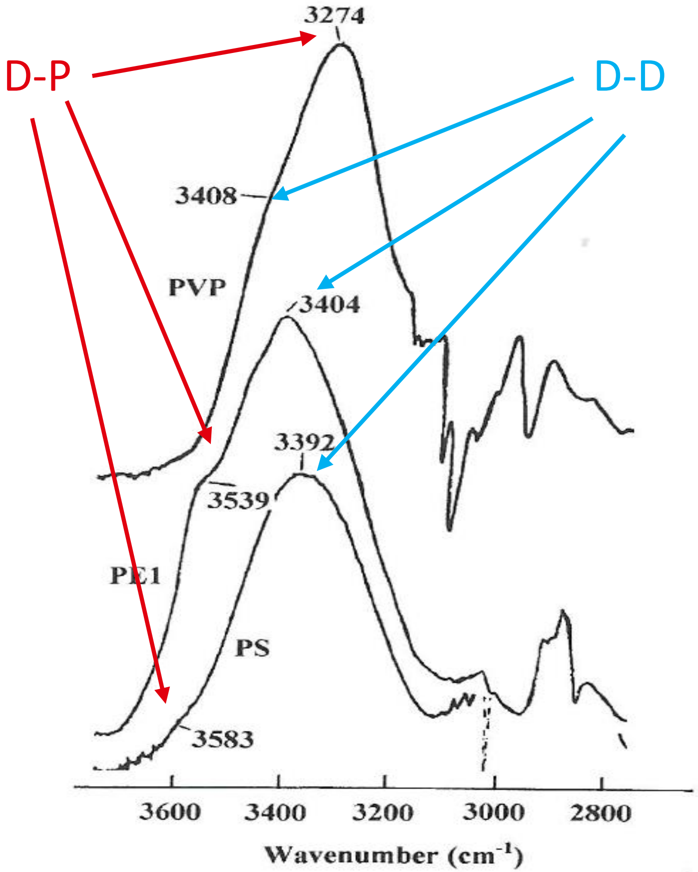
- -N= > -CON= > -CN > -COO- > -π > -Cl

D-D interaction strength

- reverse of above (small range)

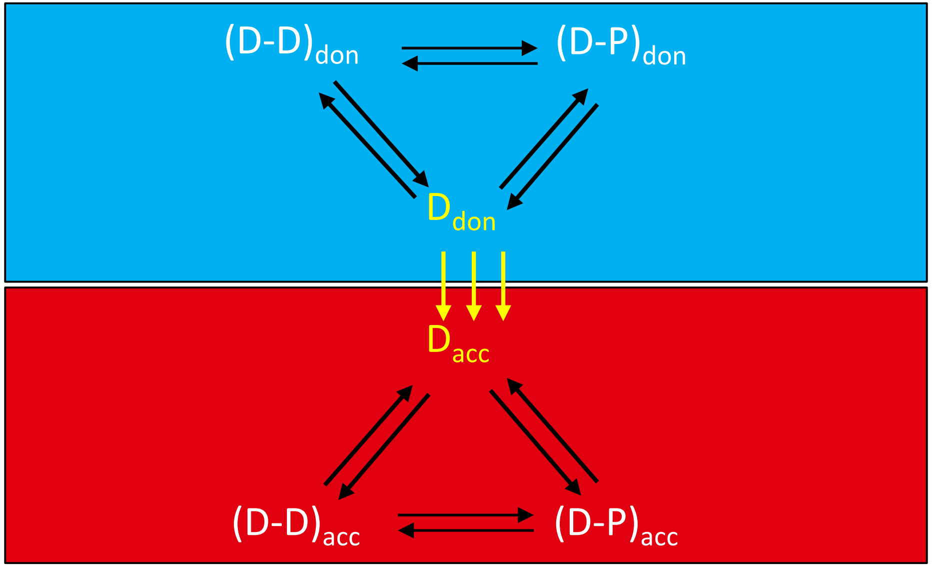
D-P: D-D ratio

- -N= > -CON= > -CN > -COO- > -π > -Cl



# Dye self-association and dye-polymer interaction

- IR shows complexity, D-D and D-P
- studies done at room temperature
- equilibria will be temperature dependent



# Conclusions

## Dye-polymer interactions in the donor layer

- dye transfer controlled by dye-polymer blend Tg
- higher Tg from stronger dye-polymer interactions and similar solubility parameters

## Dye-polymer interactions in the acceptor layer

- solution-diffusion model
- higher dye transfer from lower Tg, similar dye-solubility parameters and stronger specific dye-polymer interactions

## Dye-dye interactions…

- increase with the number of dye –OH groups
- decrease with the strength of polymer electron donor

# Acknowledgements

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# Thank you!