Polymer 40 (1999) 1325–1332

The effect of polymer structure on specific interactions between dye solutes and polymers

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Received 20 March 1998; revised 23 April 1998; accepted 23 April 1998

Abstract

The mechanism by which dye solutes specifically interact with a variety of polymer structures has been investigated. FT-i.r. spectroscopy has been used to determine the type and strength of interactions that occur between dyes containing two or three hydroxyl groups and polymers containing a range of functional groups including phenyl, chloro, cyano, carboxyl, amide and amine. Dye–polymer intermolecular interactions and dye–dye self-association interactions occur in all polymers. The relative magnitudes and strengths of these interactions depend on the types of functional group present in the polymer matrix and the concentration of the dye solute in the polymer. Solvents with analogous structures to polymer repeating units were found to give very similar dye–matrix interactions and were used to assist the identification of dye–polymer and dye–dye interactions. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Dye; Solute; Polymer; Specific interactions

1. Introduction

The behaviour of solutes in polymers is important for many industrial applications. A wide variety of additives are incorporated in polymers including plasticisers, anti-plasticisers, processing aids, lubricants and heat stabilisers [1]. Additionally, highly functional organic molecules are incorporated in polymers such as dyes for textiles or film images [2], and pharmaceuticals in drug delivery systems [3]. An important factor related to all of these applications is the physical stability of solutes in polymers which will depend on solute–polymer affinity. There are several previous papers investigating interactions between polymers and conventional plasticisers, such as phthalates, adipates and succinates [4–6]. Despite this, the number of fundamental studies on the nature of strong, specific solute–polymer interactions is limited, although the work of Jenekhe and co-workers on co-ordination complexes between polymers and inorganic solutes is noteworthy [7–9].

In contrast, there have been a substantial number of investigations into the miscibility of polymer–polymer blends [10,11]. It is well known that the miscibility of polymers is promoted by intermolecular interactions such as ion–ion, ion–dipole, dipole–dipole, donor–acceptor and hydrogen bonding [12,13]. In the past decade, significant effort has been made to understand the role of specific interactions for enhancing the miscibility and other properties of polymer–polymer mixtures. Typically, the systems investigated contain one component of the blend which self-associates and one component which does not. Additionally, the functional groups involved in hydrogen bonding interactions are different in each component. For such systems involving hydrogen-bonding and acid–base interactions, Coleman et al. [13] have developed an association model with a term dependent on the exothermic contribution of specific interactions. This has been expressed as a function of self-association and intermolecular equilibrium constants which can be determined from infra-red spectroscopy. The model has been successful in predicting phase diagrams of a variety of polymer–polymer combinations [13] and also thermal properties of polymer blends [14]. Various hydrogen-bonded polymer blends have been studied by infra-red spectroscopy, including for example poly(vinyl phenol)/poly(vinyl methyl ketone) [15], polyurethane/poly(ethylene oxide-co-propylene oxide) [16] and poly(ethylene-co-methacrylic acid)/poly(2-vinyl pyridine) [17]. The majority of infra-red studies have generally focused on the effects of interactions on the carboxyl region and have been limited to

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PII S0032-3861(98)00346-2

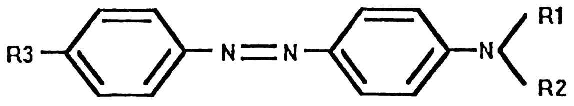
carboxyl-containing polymers where there is only one specific interaction site per polymer repeating unit.

The present paper concerns dye solute–polymer blends rather than polymer–polymer blends. In one respect, this present work is similar to previous studies on polymer–polymer blends in that one component (the dye solute) has the potential to self-associate, whereas the other (the polymer) does not. However, this work is different in that the solute investigated is multifunctional containing two or three hydroxyl groups per molecule, whereas a variety of polymers with different functional groups have been used. As a result of solute simplification and design, infra-red spectroscopy has been used to study the effects of interactions on the hydroxyl region of the solute in the infra-red spectrum rather than the polymer carboxyl group, enabling a wide variety of polymer functional groups to be investigated. Previous work on these solutes in a copolyester matrix has shown that there are dye–polymer intermolecular interactions, dye–dye self-association interactions and dye intramolecular interactions present [18]. The effects of solute concentration, the number of specific functional groups and the flexibility of the solute on these different interactions were investigated. In the work presented here, the effects of a wide variety of polymer electron-donating functional groups on the different dye solute-specific interactions has been investigated. In future publications, this information will be used to correlate solute permeability and solute stability with solute–polymer interactions [19].

It should be recognised that solute–polymer blends are inherently more compatible than polymer–polymer blends, since the relatively low molecular weight of the solute enhances the entropic contribution to miscibility. This means that it is easier to probe intermolecular interactions in polymers using solutes. Additionally, it is possible that solutes can be used as models for polymers, where the solute molecule has a similar structure to the polymer repeating unit. For example, it has been demonstrated that the infra-red absorption of functional groups in solutes are identical to those of polymer repeating units with analogous structures [20]. Therefore, in principle, the investigations in this paper are applicable to the general behaviour of both solute–polymer and polymer–polymer interactions.

2. Method

2.1. Materials used



Dye	R1	R2	R3
1	$-C_3H_6OH$	$-C_3H_6OH$	$-C_2H_4OH$
2	$-C_2H_5$	$-C_3H_6OH$	$-C_2H_4OH$
3	$-C_3H_7$	$-C_3H_7$	$-C_2H_4OH$

Fig. 1. Structures of dyes containing variations in the number of hydroxyl groups.

Fig. 1 shows the structure of the dye solutes used in this study, which were supplied by Zeneca Specialties with $> 95\%$ purity. The central part of all molecules is equivalent and consists of a simplified azo dye structure which is constant for all solutes. The only difference between the solutes is the number of functional groups on the dye which are hydroxyl groups in all cases. The functionality directly attached to the central aromatic core has been minimised so that there are no additional functional groups positioned directly on the phenyl rings. This simplification allows i.r. spectroscopy to be used to characterise dye interactions involving the hydroxyl groups.

Various polymer structures were used as matrices for the solutes, containing a wide variety of electron-donating functional groups (phenyl, chloro, cyano, carboxyl, amide and amine) and these are shown in Table 1. All polymers were used as supplied.

A number of different solvents were also used in this study including toluene, ethyl benzene, 1,3-dichlorobutane, ethyl acetate, ethyl pyrrolidone and ethyl pyridine. These were all used as supplied by Aldrich Chemical Company.

2.2. Sample preparation and infra-red spectroscopy

In order to obtain dye–polymer spectra, the appropriate dye and polymer were dissolved in spectroscopic grade tetrahydrofuran (THF, supplied by Aldrich Chemical Company) at 10% (w/w) concentration. A polymer solution was also made up at the same concentration. Drops of the two solutions were placed on separate NaCl plates, which were then dried under an i.r. lamp at 70°C for 5 min and the spectra were taken. The polymer P(VPy-co-VAc) was not soluble in THF and so ethanol was used as the solvent and BaF_2 plates were used instead of NaCl.

Dye–solvent solutions were made up at a concentration of 1% (w/w) and spectra were taken in 0.11 mm BaF_2 cells using solvent-only as a reference.

A Perkin-Elmer 1720X FTIR was used at a resolution of $2\ cm^{-1}$ and spectra were signal averaged from a minimum of 10 scans per sample to reduce noise. The polymer (or solvent) spectra were digitally subtracted from the dye–polymer (or dye–solvent) spectra with the requirement that no part of the subtracted spectra became negative. This resulted in the cancellation of polymer (or solvent)

Table 1
Summary of polymers with various functional groups

Polymer structure	Supplier	Electron-donating functional group	Abbreviation
Polystyrene	BDH Chemicals	Aromatic π-cloud	PS
Poly(vinyl chloride)	Polysciences	Halogen	PVC
Poly(vinyl acetate)	BDH Chemicals	Carboxyl	PVAc
Polyester[a]	‘Vylon 103’; Toyobo	Carboxyl	PE1
Polyester[b]	‘Vylon 200’; Toyobo	Carboxyl	PE2
Poly(methyl methacrylate)	‘Neocryl B-728’; Zeneca Specialties	Carboxyl	PMMA
Poly(methyl acrylate)	Aldrich Chemical Company	Carboxyl	PMA
Poly(ethyl methacrylate)	Aldrich Chemical Company	Carboxyl	PEMA
Poly(iso-butyl methacrylate)	‘Neocryl B-700’; Zeneca Specialties	Carboxyl	PBMA
Poly(vinyl pyrrolidone-co-vinyl acetate) 60:40 (w/w)	‘VA64’; BASF	Amide + carboxyl	P(VPy-co-VAc)
Poly(styrene-co-acrylonitrile) 75:25 (w/w)	Aldrich Chemical Company	Nitrile + π-cloud	P(S-co-AN)
Poly(styrene-co-vinyl pyridine) 20:80 (w/w)	Aldrich Chemical Company	Amine + π-cloud	P(S-co-VP)
Poly(vinyl pyridine)	Polysciences	Amine	PVP

[a] Polyester copolymer containing 25% terephthalic acid, 20% isophthalic acid, 5% sebacic acid, 25% neopentyl glycol and 25% ethylene glycol
[b] Polyester copolymer containing 25% terephthalic acid, 25% isophthalic acid, 25% neopentyl glycol and 25% ethylene glycol

peaks on the dye–polymer (or dye–solvent) spectra leaving characterisation of the dye in the polymeric (or analogous solvent) environment. The maximum absorbance of the spectra was kept below 1.0. This aided subtraction of the polymer (or solvent) by keeping the distortion of the peaks at a minimum. The method used was shown to give reproducible results and further drying of solvent and solution did not significantly affect the positions of infra-red absorptions in the O–H stretch region.

3. Results and discussion

3.1. Comparison of polymer structure to analogous solvents

The hydroxyl region in an infra-red spectrum is typically split into sub-regions depending on the type of hydrogen bond interaction occurring [21]. Free hydroxyl occurs at approximately 3630 cm^{-1}. From 3600 to 3400 cm^{-1} is a region due to hydroxyl intermolecular hydrogen bonding. This is where the dye–polymer interaction was expected to cause a peak. From 3400 to 3200 cm^{-1} is a region that is due to hydroxyl self-association, where many hydroxyl groups associate to form a hydrogen-bonded system. However, it is important to note that these boundaries are very general and are only to be used as guidelines. It is possible to have a strong intermolecular hydrogen bond producing a peak in the hydroxyl ‘self-association region’ or a weak hydroxyl self-association hydrogen-bonded system producing a peak in the ‘intermolecular region’. For example, the strong interaction between phenol and pyridine produces an intermolecular O–H stretch at 3160 cm^{-1} [22]. Previous work on hydroxyl functionalised dye solutes in a copolyester matrix has shown that the hydroxyl region contains two main species. There is a peak or shoulder in the range 3338–3421 cm^{-1} in the hydroxyl self-association region resulting from dye–dye self-association. Additionally, there is a peak or shoulder in the range 3531–3545 cm^{-1} resulting from the intermolecular hydrogen bond between the hydroxyl group on the dye and the carboxyl group on the polymer.

Low-molecular weight liquids with similar structures to

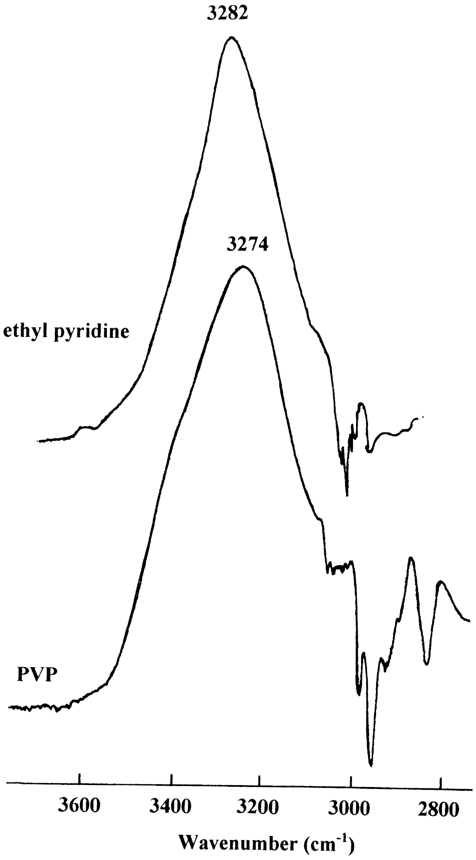


Fig. 2. Comparison of the infra-red spectra of trihydroxyl dye in PVP compared to trihydroxyl dye in the analogous solvent ethyl pyridine. The dye–solvent spectrum contains one peak. The dye–polymer spectrum contains a main peak due to dye–polymer interaction at a similar frequency to the dye–solvent peak, and a shoulder resulting from dye–dye self-association interactions.

Table 2
Comparison of bihydroxyl dye spectra in polymer and analogous solvent environments

Polymer	Analogous solvent	D–S[a] (cm^{-1})	D–P[b] (cm^{-1})
PS	Toluene	3594	3583
PS	Ethyl benzene	3600	3583
PVC	1,3-Dichlorobutane	3609	3602
PVAc	Ethyl acetate	3541	3520
P(VPy-co-VAc)	1-Ethyl, 2-pyrrolidone	3357	3368
PVP	Ethyl pyridine	3282	3279

[a] D–S is the peak absorption in the dye–solvent spectrum where the solvent is analogous to the polymer repeating unit. Values are likely to be accurate within ± 2 cm^{-1}

[b] D–P is the peak absorption in the dye–polymer spectrum resulting from dye–polymer intermolecular interaction. The estimate on precision is ± 5 cm^{-1}

the polymer repeating units were used as solvents for the dyes. The aims were to establish if solvents could be used as models for polymers and to assist with assignment of peaks in the infra-red spectra of dye–polymer samples. The infra-red spectrum of trihydroxyl dye 1 in ethyl pyridine is compared to the same dye in poly(vinyl pyridine) (PVP) in Fig. 2. This illustrates that the hydroxyl peak frequencies have similar values, suggesting that the peak in the dye–polymer spectrum is due to intermolecular dye–polymer hydroxyl-amine interaction. It is also evident that the dye–solvent spectrum produces only one peak, suggesting that only dye–solvent interaction is present. The absence of dye–dye interactions results from the dye concentration being low in the solvent (1%, w/w) in comparison to the polymer (10%, w/w), in addition to enhanced mobility of the dye in the liquid solvent. For the dye in PVP, the peak is much broader and a shoulder is evident at 3408 cm^{-1} which results from the additional dye–dye self-association interaction in the polymer matrix. Infra-red data of the bihydroxyl dye 2 in various other polymers with their analogous solvent environments are shown in Table 2. Generally, this illustrates that the dye–solvent peaks are similar in position to dye–polymer peaks, where the solvent has a similar structure to the polymer. This occurs despite the fact that in the spectra of dyes in polymers the D–P and D–D peaks are overlapping, which may be expected to produce significant errors. This point is discussed further in the next section. The comparative results between polymers and analogous solvents described here agrees with work on specific interactions in polymer–polymer blends where it has been demonstrated that solvents can be used as models for polymers [20]. There are differences, but these are relatively small in general (differences are mostly less than 10 cm^{-1}) and expected since the equivalence of solvent and polymer involves several assumptions [13]. It is assumed that unusual steric or electronic effects are not introduced moving from solvent to polymer, that specific interactions are independent of molecular weight and that the polymer chains are sufficiently flexible that hydrogen bonds can form according to their intrinsic proclivities.

3.2. The effect of solute structure at fixed concentration

The monohydroxyl, bihydroxyl and trihydroxyl solutes were compared in three different polymer matrices at a fixed concentration (10%, w/w). The matrices selected were PVC, PE1 and PVP representing the range of hydroxyl-functional group interactions from weak (hydroxyl-chlorine) to moderate (hydroxyl-carboxyl) to strong (hydroxyl-amine). The results are displayed in Table 3. D–P is the frequency of absorption resulting from intermolecular interaction between dye hydroxyl groups and polymer functional groups. D–D is the frequency of absorption resulting from dye–dye self-association interactions between hydroxyl groups. I_R

Table 3
Comparison of the infra-red spectra of monohydroxyl, bihydroxyl and trihydroxyl dyes

Dye type	Dye only	PVC			PE1			PVP		
		D–P[a]	D–D[b]	I_R[c]	D–P[a]	D–D[b]	I_R[c]	D–P[a]	D–D[b]	I_R[c]
Mono	3371	3589	3430	2.0	3543	3421	0.3	3283	—	—
Bi	3353	3602	3428	3.1	3547	3423	0.7	3279	3402	0.57
Tri	3338	3596	3387	7.2	3539	3404	1.65	3274	3408	0.62

[a] D–P is the frequency of absorption resulting from intermolecular interaction between dye hydroxyl groups and polymer functional groups (units, cm^{-1}). The estimate of precision is ± 5 cm^{-1}

[b] D–D is the frequency of absorption resulting from dye–dye self-association interactions between hydroxyl groups (units, cm^{-1}). The estimate of precision is ± 5 cm^{-1}

[c] I_R (D–D/D–P) is the intensity ratio of the D–D absorption in comparison to the D–P absorption, obtained from the relative heights of peaks or shoulders. Comparison of these ratios in different polymers should be treated with caution since there are differences in which species predominates and measuring heights of shoulders introduces large errors due to overlapping peaks

(D–D/D–P) is the intensity ratio of the D–D absorption in comparison to the D–P absorption, obtained from the relative heights of peaks or shoulders. The dye–polymer absorption frequencies for the three dyes appear to differ in the same matrix (8–13 cm^{-1}, depending on the matrix). However, for particular systems, the precise location of dye–polymer absorption is more difficult since this occurs as a shoulder and not a peak due to overlap with a larger peak resulting from dye–dye self-association. Also, the level of self-association is systematically higher for the trihydroxyl dye resulting in less-pronounced shoulders or peaks which introduces further error. Additionally, the resolution of the instrument is 2 cm^{-1} in comparison to the small changes which do not vary systematically as the number of hydroxyl groups increases. Therefore, it can be concluded that the peak frequencies resulting from dye–polymer interactions are similar in the same polymer, independent of the number of hydroxyl groups. A general point worth noting is that it is recognised that the D–P and D–D peaks are strongly overlapping. The peak value for the predominant species is likely to be reasonably precise, within the resolution of the instrument ($\pm 2\ cm^{-1}$). However, values assigned to shoulders which result from the relatively minor species are likely to be subject to more error ($\pm 5\ cm^{-1}$). As previously described, there is very good correlation between the D–P absorption (which could potentially be perturbed by the overlapping D–D absorption) and the absorption of dye in a solvent, where the solvent has an analogous structure to the polymer repeating unit and D–D interactions are absent. This suggests that the D–P values are more precise than may be expected given the overlapping nature of the D–P and D–D peaks.

For all polymers, the dye–dye self-association for a particular solute occurs at a higher frequency compared to the dye-only spectra indicating that dye–dye self-association is weaker in the presence of the polymer. In all polymers, this peak grows in size relative to dye–polymer interactions, as the number of hydroxyl groups increases. The absolute frequencies of dye–dye absorption are similar for the monohydroxyl and bihydroxyl solute in a particular matrix, but the strength of dye–dye self-association increases for the trihydroxyl solute since the dye–dye peak moves to lower frequencies. For mono-, bi- and trihydroxy solutes, the dye–dye interaction is the predominant absorption in the weakly interacting PVC, and occurs as the main peak which grows in size as the number of hydroxyl groups increases ($I_R \gg 1$). However, for the strongly interacting PVP, the dye–polymer interaction is the predominant absorption for all solutes ($I_R < 1$ for mono-, bi- and trihydroxyl). This occurs to such an extent that dye–dye absorption cannot be determined for the monofunctional solute.

3.3. The effect of polymer structure at fixed concentration

Table 3 also shows the effect of changing polymer structure for the mono-, bi- and trihydroxyl dyes. The relative effects of polymer structure are similar for each solute type, although the level of dye–polymer interaction (compared to dye self-association) increases as the number of hydroxyl groups reduces. The effect of polymer structure is best exemplified by the spectra of trihydroxyl dye in polystyrene, polyester and poly(vinyl pyridine) which are illustrated in Fig. 3. These polymers represent different environments which form weak (hydroxyl-π-cloud), moderate (hydroxyl-carboxyl) and strong (hydroxyl-amine) dye–polymer hydrogen bond interactions, respectively. In the weakly interacting polystyrene, the spectrum is dominated by dye–dye self association (3392 cm^{-1}) with a very small amount of dye–polymer interaction (3583 cm^{-1}). Additionally, the dye–dye interaction is stronger than the dye–polymer interaction, since the peak frequency is lower for the former absorption. For the moderately interacting polyester, the dye–dye self-association still predominates (3404 cm^{-1}), but the dye–polymer interaction (3539 cm^{-1}) becomes more evident as a pronounced shoulder. The relative amount of self-association remains higher and also the dye–dye self-association interaction continues to be stronger than the dye–polymer intermolecular interaction, since the peak frequency for the former remains lower. However, the situation changes in the strongly interacting PVP. In this matrix, it is now the dye–polymer interaction which predominates to such an extent that it becomes the main peak (3274 cm^{-1}) with the dye–dye self-association being

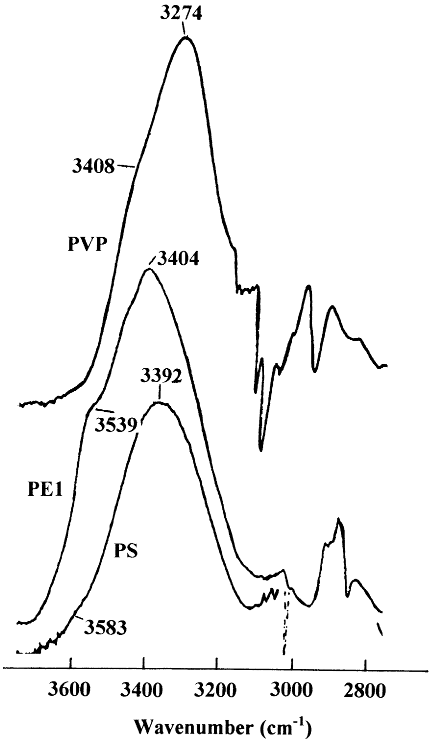


Fig. 3. Comparison of the infra-red spectra of trihydroxyl dye in PS, PE1 and PVP. The dye–polymer interaction increases in strength and magnitude as the strength of the electron-donating functional group increases, whereas the dye–dye self-association interaction decreases in strength and magnitude.

inferior, appearing as a shoulder (3408 cm^{-1}). Progressing along the series from low–moderate–high polymer electron donor strength, the strength of the intermolecular dye–polymer interaction consistently increases since the dye–polymer peak shifts to lower frequencies (3583, 3539 and 3274 cm^{-1} in PS, PE1 and PVP, respectively). Along the same series, the strength of the dye–dye self-association decreases since the dye–dye peak moves to higher frequencies (3392, 3404 and 3408 cm^{-1} in PS, PE1 and PVP, respectively). The effect of environment on the dye–polymer interaction (range 309 cm^{-1}) is considerably greater than its effect on dye–dye interaction (range 16 cm^{-1}) with the latter variation being only just outside experimental error.

The effects of all polymer structures investigated on the various interactions are displayed in Table 4 for the bihydroxyl solute at a concentration of 10% (w/w). There is a consistent reduction in solute O–H frequency and concomitant elevation in the strength of the dye–polymer interaction as the strength of electron donor polymer functional groups increases along the series –Cl, π, –COO–, –CN, –CON–, –N=. The absolute frequencies obtained for a particular dye hydroxyl–polymer functional group combination are similar to those in the literature for methanol or ethanol in combination with low-molecular weight solvents containing different functional groups [23]. This further substantiates the point that the frequencies quoted are likely to be reasonably precise despite the potentially significant errors which may be introduced due to the nature of the overlapping peaks. The amide and amine environments are the only two matrices where the dye–polymer interactions are stronger (OH at a lower frequency) than the dye–dye self-association. Polymers which have similar functional groups produce very similar absorption frequencies resulting from dye–polymer interactions; e.g. for the various polyester, polymethacrylate, polyester and vinyl polymers with carboxyl groups, the dye–polymer interaction frequency remains fairly consistent in the range 3541–3547 cm^{-1} with the exception being PVAc (3520 cm^{-1}), suggesting a stronger interaction in this case. For the bihydroxyl solute, the peak resulting from dye–polymer interaction is consistently larger than the peak due to dye–dye interaction ($I_R < 1$), except for PS and PVC. For both of these polymers, the dye–polymer peak is very small and at a high frequency indicating a very weak interaction.

It is difficult to gain further insights from the intensity ratios due to the overlapping peaks, the variation in whether dye–polymer interaction or dye–dye interaction predominates and the changes in the relative positions of these two absorptions. Nevertheless, the effect of the environment on interaction strength is much larger for dye–polymer interactions than dye–dye self-association; the frequency range for absorption is 3602–3279 cm^{-1} ($\Delta = 323\ \mathrm{cm}^{-1}$) for D–P and 3400–3436 cm^{-1} ($\Delta = 36\ \mathrm{cm}^{-1}$) for D–D. For the bihydroxyl solute in the wide variety of polymers, the position of the dye–dye self-association peak does not vary systematically as the electron donating strength of the polymer environment increases. This may result from the dye–dye absorption generally appearing as a minor species (shoulder) rather than a main peak (apart from PS and PVC where it is the main peak). The position of the absorption resulting from dye–dye self-association (3400–3435 cm^{-1}, depending on the polymer type) is significantly weaker than the self-association of the bihydroxyl dye-only in the absence of polymer (not illustrated, peak absorption 3353 cm^{-1}). The latter is typical of hydroxyl self-association in other materials and, for example, is similar to the peak absorption of 3360 cm^{-1} in poly(vinyl phenol) [24] and 3344 cm^{-1} in poly(vinyl alcohol) [25].

Table 4
Infra-red characterisation of bihydroxyl dye in various polymers at a concentration of 10% (w/w)

Polymer	Functional group	D–P[a] (cm^{-1})	D–D[b] (cm^{-1})	I_R(D–D/D–P)[c]
PVC	–Cl	3602	3428	3.13
PS	–Phenyl	3583	3400	3.13
PBMA	–COO–	3544	3423	0.65
PE1	–COO–	3547	3425	0.70
PE2	–COO–	3547	3421	0.81
PMMA	–COO–	3541	3425	0.74
PEMA	–COO–	3541	3421	0.64
PMA	–COO–	3541	3429	0.46
PVAc	–COO–	3520	3435	0.77
P(S-co-AN)	–CN, -phenyl	3518	3436	0.92
P(VPy-co-VAc)	–CON–, –COO–	3368	3429	0.91
P(VP–co–S)	–N=, phenyl	3281	3415	0.64
PVP	–N=	3279	3402	0.57

[a] D–P is the frequency of absorption resulting from intermolecular interaction between dye hydroxyl groups and polymer functional groups. The estimate of precision is ± 5 cm^{-1}

[b] D–D is the frequency of absorption resulting from dye–dye self-association interactions between hydroxyl groups. The estimate of precision is ± 5 cm^{-1}

[c] I_R (D–D/D–P) is the intensity ratio of the D–D absorption in comparison to the D–P absorption, obtained from the relative heights of peaks or shoulders. Comparison of these ratios in different polymers should be treated with caution since there are differences in which species predominates and measuring heights of shoulders introduces large errors due to overlapping peaks

3.4. The effect of polymer structure and varying concentration

The concentration dependence of the specific interactions of trihydroxyl dye 1 in the different environments PS, PE1, PVAc and P(VPy-co-VAc) has been investigated in the concentration range 1–16% (w/w). The results for the dye–polymer intermolecular interactions and dye–dye self-association interactions are shown in Table 5. The results are similar to previous work reported for trihydroxyl solute in polyester only [18]. The absolute positions of absorption for the various species depend on the nature of the matrix but for PS, PE1, PVAc and P(VPy-co-VAc), the dye–polymer frequency does not vary greatly as a function of concentration. The results at very low solute concentration will be prone to more error due to the fact that subtraction of polymer only is not perfect. Considering this in addition to overlapping peaks it is likely that these changes (which are relatively small in comparison to the effect of concentration on D–D) can be explained by experimental error, resulting in the conclusion that dye–polymer interaction strength does not vary substantially with dye concentration to a first approximation. For all matrices, the dye–dye peak grows in intensity relative to the dye–polymer peak (not illustrated) and the position of the dye–dye peak is significantly concentration dependent. For the latter, the hydroxyl frequency decreases in frequency (by 30–100 cm^{-1} depending on the environment) as the concentration increases indicating an increasing strength of the self-association interaction. The strength of dye–polymer interaction increases in the order PS $<$ PVAc $<$ P(VPy-co-VAc), which agrees with the previous results at fixed concentration discussed earlier, but the strength of dye–dye self-association increases in the reverse order, i.e. PVAc $<$ PS (no peak was obtainable for P(VPy-co-VAc) due to overlap of dye–polymer and dye–dye peaks for this material). This reversed trend can be explained by the concentration dependence of the dye–dye self-association peak. A strongly interacting polymer favours dye interacting with polymer rather than other dye molecules. This leads to a smaller amount of dye self-associating which leads to a weaker dye–dye interaction due to the concentration dependence of the latter. Hence, a strong dye–polymer interaction leads to a weak dye–dye self-association interaction and vice versa.

4. Conclusions

The interactions of hydroxyl functionalised dye solutes in various polymers have been investigated. Simplification of solute structure has allowed FT-i.r. spectroscopy to be a useful tool in determining the nature and extent of different types of solute interactions. There are two main species present which occur in all systems, independent of the type of electron-donating functional groups on the polymer. These are the dye–polymer intermolecular interaction between the dye hydroxyl group and the polymer electron-donating functional group, and the dye–dye self-association interaction between dye hydroxyl groups.

The strength of the dye–polymer interaction is independent of the number of hydroxyl groups present in the dye solute. There is a close correlation between the strength of a dye–polymer interaction and the strength of a dye–solvent interaction, where the dye is constant and the solvent has a structure which is analogous to the polymer repeating unit. The use of solvents as models for polymers assists in identification of absorptions resulting from dye–polymer and dye–dye interactions in the spectra of solid-state samples, since dye self-association interactions are absent in the solvents at low concentration.

For trihydroxyl dye solute, the D–D self-association interaction is usually the main species with D–P being the minor species, apart from an amine environment where interactions are strong and D–P becomes the major species. For bihydroxyl dye solute, where the potential for D–D self-association is reduced, the D–P intermolecular interaction is usually the main species with D–D being the minor species. The exceptions to this are the weakly interacting phenyl and chloro environments where D–D is the primary component.

At a fixed concentration, the acid–base interaction between dye and polymer becomes stronger and more

Table 5
The effect of dye concentration on the positions of D–P and D–D absorptions

Concentration (w/w%)	D–P[a] (PS) (cm^{-1})	D–P[a] (PE1) (cm^{-1})	D–P[a] (PVAc) cm^{-1}	D–P[a] (P(VPy-co-VAc)) (cm^{-1})	D–D[b] (PS) (cm^{-1})	D–D[b] (PE1) (cm^{-1})	D–D[b] (PVAc) (cm^{-1})
1	3585	3545	3535	3416	3439	3432	3457
5	3585	3543	3531	3406	3392	3421	3447
10	—	3539	3521	3387	3385	3404	3431
16	—	3537	3498	3386	3362	3368	3429

[a] D–P is the frequency of absorption resulting from intermolecular interaction between dye hydroxyl groups and polymer functional groups. The estimate of precision is ± 5 cm^{-1}

[b] D–D is the frequency of absorption resulting from dye–dye self-association interactions between hydroxyl groups. The estimate of precision is ± 5 cm^{-1}

favourable as the strength of electron donor in the polymer increases along the series $-\mathrm{Cl} < -\pi < -\mathrm{COO}- < -\mathrm{CN} < -\mathrm{CON}= < -\mathrm{N}=$. The amide and amine environments are the only cases where the dye–polymer interactions are stronger than the dye–dye self-association. There is some evidence that the strength of the dye–dye self-association interaction decreases as the electron-donating group increases in strength due to the concentration dependence of the dye–dye interaction, but this variation is not systematic and relatively small.

Although absolute values depend on the nature of the polymer matrix, within a variety of polymers the strength of dye–polymer interaction does not vary substantially with dye concentration. In comparison, the dye–dye self-association interaction is particularly concentration dependent with a higher concentration producing a higher degree of self-association. At low solute concentrations the dye–polymer interaction predominates but the dye–dye self-association interaction becomes more favourable as concentration increases.

Acknowledgements

The authors would sincerely like to thank Alan Butters (ICI Imagedata) for a number of useful discussions which occurred during the course of this work. In particular, we appreciate the help and advice of Peter Winter (ICI Imagedata) in using the FT-i.r. spectrometer. We would also like to acknowledge the skills of Roy Bradbury and Clive Mosscrop (Zeneca Specialties) for the dye synthesis and characterisation. Finally, we would like to thank Robert Glen (ICI Imagedata) for allowing publication of this work.

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