

Specific interactions between dye solutes and polymers: The effect of dye solute structure and concentration

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An investigation has been performed to determine the mechanism by which dye solutes specifically interact in an amorphous copolyester matrix. Using FTi.r. spectroscopy it has been possible to determine both the type and strength of interactions that occur between dyes containing hydroxyl groups and a copolyester containing electron-donating carboxyl functional groups. Dye–polymer intermolecular interactions, dye–dye self-association intermolecular interactions and dye intramolecular interactions have been identified. The dye structures were simplified and changed systematically, enabling the effects of solute concentration, the number of solute hydroxyl groups and the flexibility of the solute molecule to be established on the various interactions. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The behaviour of solutes in polymers is important in many industrial applications. A wide variety of additives are incorporated in polymers including plasticisers, anti-plasticisers, processing aids, lubricants and heat stabilisers¹. Additionally, highly functional organic molecules are incorporated in polymers such as dyes for textiles or film images², and pharmaceuticals in drug delivery systems³. An important factor related to all of these applications is the physical stability of solutes in polymers and this depends on solute–polymer affinity to a large extent. There are previous examples where interactions between polymers and conventional plasticisers such as phthalates, adipates and succinates have been investigated^{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 *et al.* 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}. This has arisen as a consequence of both fundamental interest and industrial application. The mixing of polymers is unfavourable due to the low entropy of mixing and can lead to phase separation. However, 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 in 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 and Painter *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 (i.r.) spectroscopy. The model has been successful in predicting phase diagrams of a variety of polymer–polymer combinations¹³ and also thermal properties of polymer blends¹⁴. Various hydrogen-bonded polymer blends have been studied by i.r. spectroscopy, including for example poly(vinyl phenol)/poly(vinyl methyl ketone)¹⁵, polyurethane/poly(ethylene oxide–copropylene oxide)¹⁶ and poly(ethylene–co-methacrylic acid)/poly(2-vinyl pyridine)¹⁷. The majority of i.r. studies have generally focused on the effects of interactions on the carboxyl region and have been limited to polymers where there is only one specific interaction site per polymer repeating unit.

The present paper concerns 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 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 one to three hydroxyl groups per molecule whereas the polymer is a polyester containing two carboxyl groups per repeating unit. As a result of solute simplification and design, i.r. spectroscopy has been used to study the effects of interactions on the hydroxyl region of the solute in the i.r. spectrum rather than the polymer carboxyl group (which has predominantly been the focus of study in polymer–polymer blends). Additionally, i.r. spectroscopy has been used to study the effects of solute concentration, the number of specific functional groups and the flexibility of the solute on the interactions present.

It should be recognised that solute–polymer blends are inherently more compatible than polymer–polymer blends,

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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 i.r. absorption of functional groups in solutes is identical to those of polymer repeating units with analogous structures¹⁸. Therefore, in principle, the investigations in this paper are applicable to the general behaviour of both solute-polymer and polymer-polymer interactions.

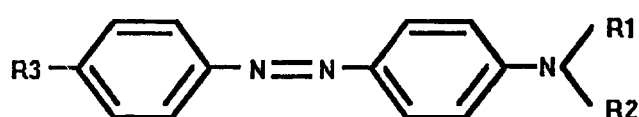
METHOD

Material used

Figure 1 shows the structure of all dye solutes used in this study which were supplied by Zeneca Specialities 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 differences between the solutes are the length of alkyl chain spacer group between the chromophore and the peripheral functionality (compare dyes 1-4), or the number of functional groups on the dye which are hydroxyl groups in all cases (compare dyes 1, 5 and 6). 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. The polymer used in this work was an aromatic polymer copolymer 'Vylon 103', obtained from Toyobo, containing 20% isophthalic acid, 25% terephthalic acid, 5% sebacic acid, 25% neopentyl glycol and 25% ethylene glycol.

Sample preparation and i.r. spectroscopy

In order to obtain spectra of dye alone, dye was deposited on a sodium chloride plate by evaporating solvent from a dilute dye solution, using an i.r. lamp at 70°C for 5 min. In



Dye	R1	R2	R3
1	-C ₃ H ₆ OH	-C ₃ H ₆ OH	-C ₂ H ₄ OH
2	-C ₄ H ₈ OH	-C ₄ H ₈ OH	-C ₂ H ₄ OH
3	-C ₅ H ₁₀ OH	-C ₅ H ₁₀ OH	-C ₂ H ₄ OH
4	-C ₇ H ₁₄ OH	-C ₇ H ₁₄ OH	-C ₂ H ₄ OH
5	-C ₂ H ₅	-C ₃ H ₆ OH	-C ₂ H ₄ OH
6	-C ₃ H ₇	-C ₃ H ₇	-C ₂ H ₄ OH

Figure 1 Structures of dyes containing variations in the number of hydroxyl groups and/or lengths of alkyl chain spacer units between the peripheral hydroxyl groups and the central aromatic delocalised core

order to obtain dye-polymer spectra, the appropriate dye and polymer were then dissolved in spectroscopic grade tetrahydrofuran (THF, supplied by Aldrich Chemical Company) at a 10% (w/w) concentration. A solution of polymer only 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 was taken.

A Perkin-Elmer 1720X FTi.r. 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 pure polymer spectra were digitally subtracted from the dye-polymer spectra with the requirement that no part of the subtracted spectra became negative. This resulted in the cancellation of polymer peaks on the dye-polymer spectra, producing characterisation of the dye in the polymeric environment. The maximum absorbance of the spectra was kept below 1.0 by altering the thickness of layer deposited on the plates. This aided subtraction of the polymer spectra by keeping the distortion of the peaks to 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 i.r. absorptions in the O-H stretch region.

RESULTS AND DISCUSSION

Types of interaction

The hydroxyl region in an i.r. spectrum is typically split into sub-regions depending on the type of hydrogen bond interaction occurring¹⁹. Free hydroxyl occurs at approximately 3630 cm⁻¹. From 3600 to 3400 cm⁻¹ is a region that is 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, resulting from many hydroxyl groups associating 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

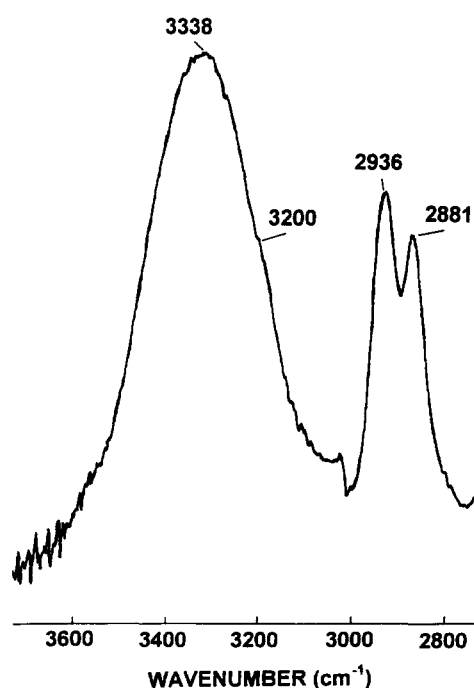


Figure 2 Infra-red spectrum of tri-hydroxyl dye 1

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} ²⁰.

The spectrum of pure tri-hydroxyl dye 1 is shown in *Figure 2*. The hydroxyl region is dominated by a large, broad peak at 3338 cm^{-1} with a shoulder at 3200 cm^{-1} . The peak at 3338 cm^{-1} is in the hydroxyl self-association region and is due to dye-dye association which results from the trifunctionality. The position of this absorption is typical of hydroxyl self-association in other materials and similar to 3360 cm^{-1} in poly(vinyl phenol)²¹ and 3344 cm^{-1} in poly(vinyl alcohol) for example²². The shoulder at 3200 cm^{-1} results from intramolecular bonding in the dye between the hydroxyl group and tertiary amino group. The spectrum of tri-hydroxyl dye 1 in polyester is illustrated in *Figure 3* at a number of dye concentrations. It is immediately obvious that there is more than one peak contributing to the spectrum in the hydroxyl region. Focusing on the spectrum at 10% (w/w) there is a large peak at 3404 cm^{-1} but there is also a distinct shoulder at 3539 cm^{-1} and a slight shoulder at 3200 cm^{-1} (the latter is more evident at lower concentrations). These two shoulders are caused by smaller peaks overlapping the dominant peak at 3404 cm^{-1} . The presence of three peaks (manifested as one actual peak and two shoulders) indicates that the hydroxyl groups are subject to three different environments,

i.e. that there are three types of interaction occurring. Referring to hydroxyl regions discussed previously and the spectrum of pure dye in *Figure 2*, it is possible to assign the types of interaction which are causing the peaks. The peak at 3404 cm^{-1} is due to hydroxyl association. Since only the dye contains hydroxyl groups, hydroxyl self-association implies that there is dye self-association and the 3404 cm^{-1} peak is due to that environment. The absorption due to dye self-association in the presence of polymer is in a similar region of the spectrum as the pure dye, but the position is different, being 3404 cm^{-1} in the former but 3338 cm^{-1} in the latter. This results from the fact that dye self-association is weaker in the presence of polymer as a result of the additional dye-polymer interaction. The shoulder at 3200 cm^{-1} results from intramolecular bonding between the hydroxyl group and the tertiary amino group since it is in the same position as for pure dye and does not depend on concentration. The peak at 3539 cm^{-1} is in the intermolecular hydrogen bond region and is due to the intermolecular hydrogen bond formed between the hydroxyl group on the dye and the carboxyl group on the polymer, i.e. it is due to the dye-polymer interaction. Previous studies have shown that in the interactions of alcohols with esters, the intermolecular hydrogen bond produces absorption in this region²³. In our work, a dye-solvent spectrum was compared to a dye-polymer spectrum where the structures of the solvent and the polymer repeat unit were similar, the solvent being ethyl acetate and the polymer being poly(vinyl acetate). The O-H stretch in ethyl acetate was 3540 cm^{-1} in comparison with 3535 cm^{-1} in poly(vinyl acetate). This confirms that the absorption at 3539 cm^{-1} in the dye-polyester combination is a result of intermolecular dye-polymer interaction between hydroxyl and carboxyl groups. It is also noticeable that a peak in the free hydroxyl region is absent in the spectrum, indicating that all of the hydroxyl groups are involved in one of the interactions described.

The effect of dye concentration

The spectra of tri-hydroxyl dye 1-polyester combinations were analysed at six different concentrations, ranging from 1 to 60% (w/w). As the concentration changes there are differences in both intensity and frequency of the peaks that help with the peak assignment. *Figure 3* illustrates the effect of solute concentration (1-10% (w/w)) on the relative intensities of dye-polymer and dye-dye interactions. The data for the whole concentration range are reproduced in *Table 1*, which also includes the intensity ratio of dye-polymer and dye-dye absorption peaks. At high concentrations, the dye-dye self-association peak predominates, as shown by the low dye-polymer/dye-dye ratio. Indeed, the dye-dye peak at 60% (w/w) dye is so large as to make accurate readings of the frequency of the dye-polymer peak impossible. As the dye concentration decreases the dye-dye peak decreases in intensity relatively to the dye-polymer peak and the ratio increases accordingly. At a dye concentration of 5% (w/w) it is the dye-polymer peak which predominates. This is consistent with the fact that at low dye concentrations there is only a small number of dye molecules in comparison with the mass of polymer present. Therefore, a single dye molecule is more likely to interact with the polymer rather than the low population of dye molecules and consequently at low concentrations most of the interactions are dye-polymer in nature. It should be noted that at this low concentration, the frequency values will be subject to a greater error because of the difficulty in

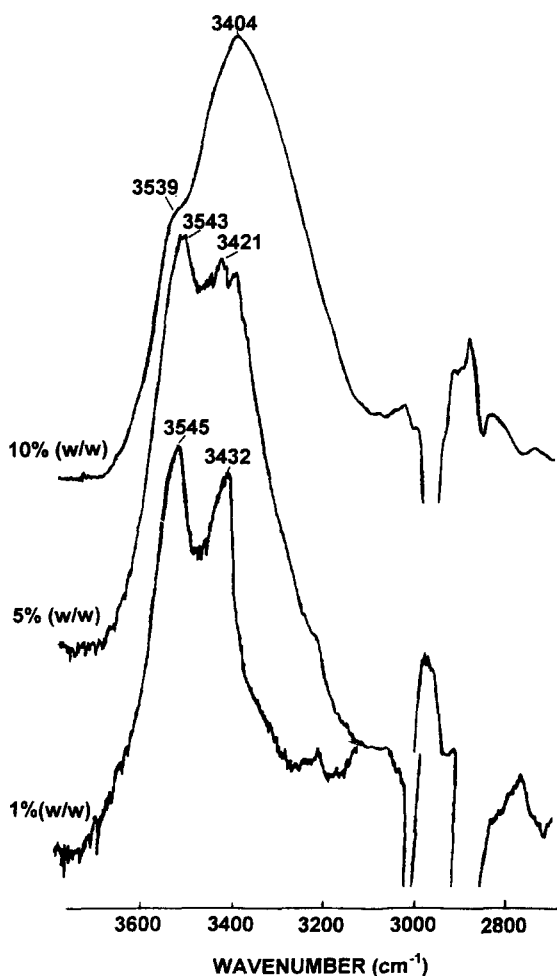


Figure 3 Infra-red spectra of tri-hydroxyl dye 1 in polyester at concentrations of 1% (w/w), 5% (w/w) and 10% (w/w)

Table 1 Peak frequencies and intensity ratios for tri-hydroxyl dye 1 in polyester at various concentrations

Concentration (%) (w/w)	D-P ^a (cm ⁻¹)	D-D ^b (cm ⁻¹)	I _R (D-P/D-D) ^c
1	3545	—	—
5	3543	3421	1.05
10	3539	3404	0.62
16	3537	3368	0.40
30	3531	3344	0.38
60	—	3344	0.23 ^d

^aD-P is the frequency of absorption resulting from intermolecular bonding between dye hydroxyl groups and polyester carboxyl groups.

^bD-D is the frequency of absorption resulting from dye-dye self-association interactions between hydroxyl groups.

^cI_R (D-P/D-D) is the intensity ratio of the D-P absorption in comparison with the D-D absorption.

^dThe D-P frequency was difficult to establish; therefore, the I_R (D-P/D-D) for this concentration is a rough estimate.

obtaining adequate subtraction of the polymer-only spectra from the dye-polymer spectra.

The dye-dye peak shows strong concentration dependence with a frequency of 3344 cm⁻¹ at high concentrations which then increases to 3421 cm⁻¹ as the concentration drops to 5% (w/w), indicating a weakening of the hydrogen bonded system with lower concentrations. This is consistent with a greater proportion of dye-polymer interaction at lower concentrations. The frequency of the dye-dye interaction is asymptotic to approximately 3340 cm⁻¹ as the concentration tends to 100%, which is very similar to the frequency of absorption in the pure dye spectrum (3338 cm⁻¹) corresponding to the maximum strength of dye-dye interaction in the absence of polymer host. In comparison, the dye-polymer peak has a frequency which remains remarkably constant through the concentration range, varying from 3545 to 3532 cm⁻¹ (1–30%). This variation is small considering the resolution of the instrument, the difficulty in pinpointing the position of the shoulder absorption and the subtraction method introducing errors at low concentration. As noted previously, the position of the intramolecular peak at 3200 cm⁻¹ remains constant, independent of concentration but it is difficult to comment on its magnitude since the absorption is weak with significant overlap.

The overall picture is that dye intramolecular interactions are present at all concentrations and are unaffected by concentration. As the concentration changes the dye-polymer interaction remains at the same frequency, suggesting that although the amount of dye-polymer interaction is reduced, the mechanism of interaction is unaffected by concentration. As concentration increases, the magnitude of dye-dye interaction increases and the mechanism changes. There will be a distribution of the number of dye molecules associating but it is likely that the average number of molecules involved will increase, leading to an increase in size and strength of the hydrogen bonded system.

The effect of solute functional groups

The effect of varying the number of hydroxyl groups from one to three was investigated and the i.r. spectra of pure dyes are illustrated in Figure 4. For the dye spectra, there is a large dye-dye peak with mono-, bi- and tri-functional solutes which increase in magnitude and decrease in frequency (from 3371 to 3338 cm⁻¹) as the number of hydroxyl groups increases. This is consistent with a higher degree of self-association and an increased strength of

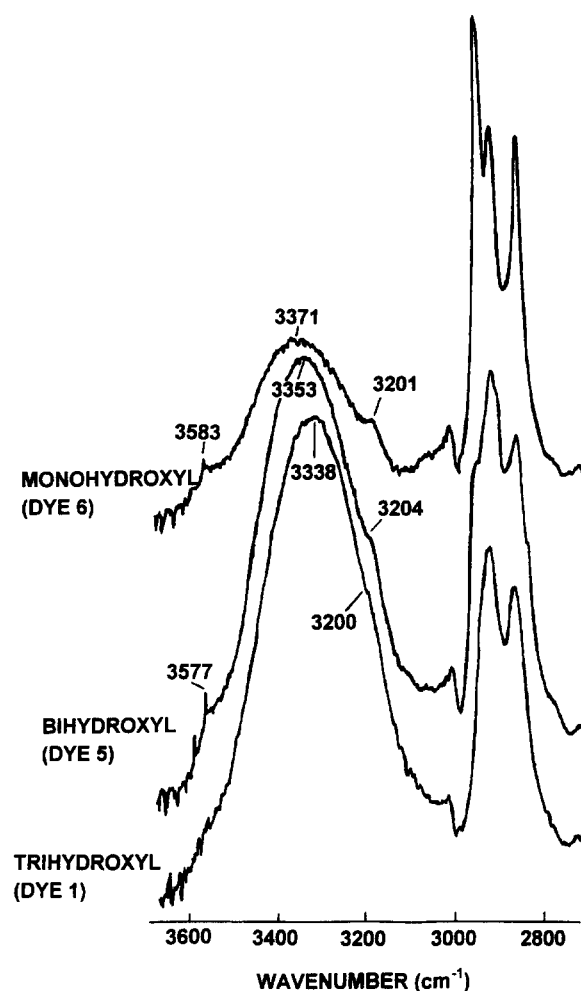


Figure 4 Infra-red spectra of dyes with one, two and three hydroxyl groups

interaction. It is interesting to note the changes in the alkyl region as the methyl C-H peak at 2960 cm⁻¹ becomes less evident in the bi-hydroxyl dye spectra (in comparison with the peak resulting from dye-dye self-association) and especially in the tri-hydroxyl dye spectra due to the increased degree of hydroxyl association. The intramolecular peak is present at 3200 cm⁻¹, independent of the number of functional groups. For the bi- and mono-hydroxyl dyes there is a shoulder at 3580 cm⁻¹ which is also likely to be present for the tri-hydroxyl dye but is obscured by the increased size of the dye-dye peak. The position of this peak is similar to absorption reported between alcohol and benzene²² and is likely to result from a weak hydrogen bond between the dye hydroxyl group and the π -electrons in the delocalised aromatic core.

The spectra of mono-, bi-, and tri-hydroxyl dyes in polyester are shown in Figure 5, and are governed by the same principles as discussed previously. The tri-hydroxyl dye spectrum is dominated by the large dye-dye peak at 3404 cm⁻¹ (data reproduced in Table 2) with the dye-polymer peak evident as a shoulder at 3539 cm⁻¹. With the bi-hydroxyl, the ability for the dye to self-associate is reduced resulting in the dye-dye peak decreasing in intensity and increasing in frequency, indicating weaker interaction. The dye-polymer peak remains at the same frequency as the tri-hydroxyl dye but it is now a true peak rather than a shoulder on the dye-dye peak. This is also true for the intramolecular peak at 3200 cm⁻¹. These effects are increased with the mono-hydroxyl spectra, with the

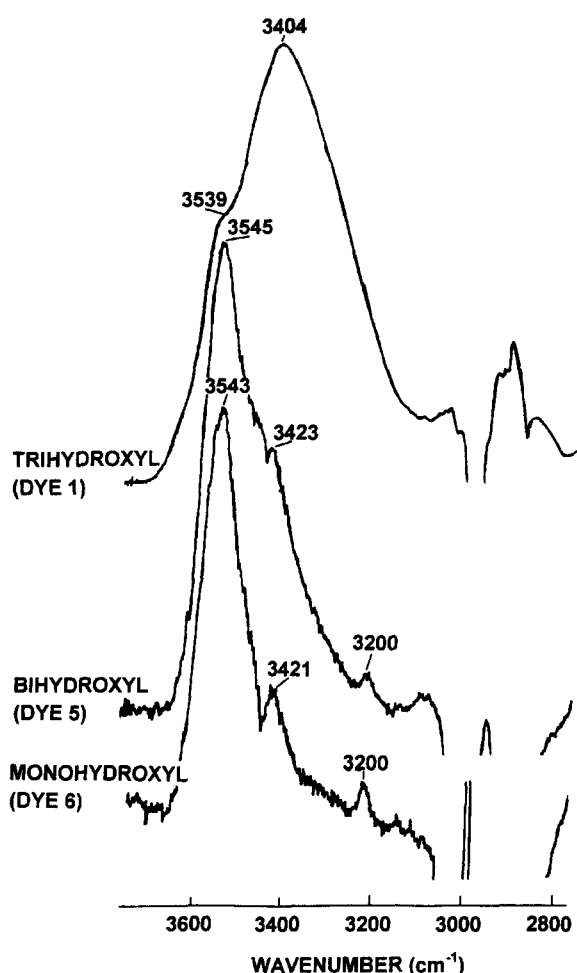


Figure 5 Infra-red spectra of mono-hydroxyl, bi-hydroxyl and tri-hydroxyl dyes in polyester at a concentration of 10% (w/w)

Table 2 The effect of dye structure on peak frequencies and intensity ratios for various dyes in polyester at a concentration at 10% (w/w)

No. of hydroxyl groups	R1 and R2 spacer length ^a	D-P ^b (cm ⁻¹)	D-D ^c (cm ⁻¹)	I_R (D-P/D-D) ^d
1	-	3543	3421	3.00
2	-C3-	3545	3423	1.75
3	-C3-	3539	3404	0.59
3	-C3-	3535	3400	0.63
3	-C4-	3535	3389	0.53
3	-C5-	3537	3396	0.54
3	-C7-	3535	3391	0.61

^aThe spacer length for R3 is constant at -C2- for all dyes.

^bD-P is the frequency of absorption resulting from intermolecular bonding between dye hydroxyl groups and polyester carboxyl groups.

^cD-D is the frequency of absorption resulting from dye-dye self-association interactions between hydroxyl groups.

^d I_R (D-P/D-D) is the intensity ratio of the D-P absorption in comparison with the D-D absorption.

^eOnly R1 has a spacer since R2 is an alkyl group with no hydroxyl.

dye-dye peak being further reduced in intensity, leaving the dye-polymer peak even more prominent. In this case, changing from two to one hydroxyl groups does not significantly affect the position of either absorption due to the dye-polymer or the dye-dye interactions.

The effect of solute flexibility

The interactions of four tri-hydroxyl solutes were compared, the difference between the molecules being the length of the alkyl chain spacer between the central delocalised aromatic core and the peripheral hydroxyl groups. The spectra of pure solutes, illustrated in Figure 6, are very similar. The dye-dye peak is constant throughout (3336–3339 cm⁻¹, within the accuracy of the method), suggesting that the interaction strength for dye-dye self-association is the same, independent of steric and entropic factors which the variation in alkyl chain length will provide. The only notable difference in the spectra is the growth of the methylene C-H peak in comparison with the hydroxyl peak as the length of the spacer group increases. The i.r. absorptions for the four solutes in polyester at the same concentration are also similar, as illustrated in Table 2. Within experimental error, the dye-dye interaction is approximately constant at 3395 cm⁻¹ and the dye-polymer interaction peak is constant at 3535 cm⁻¹. The largest variation appears in the dye-dye absorption frequency (3389–2400 cm⁻¹) but this is small. Additionally, the dye-polymer/dye-dye intensity ratio is also reasonably consistent. Therefore, changing the spacer length of the dyes in the range C₃ to C₇ does not have any effect on the dye interactions and altering the chain length does not restrict the relative capabilities of the dye to self-associate or interact with the polyester host.

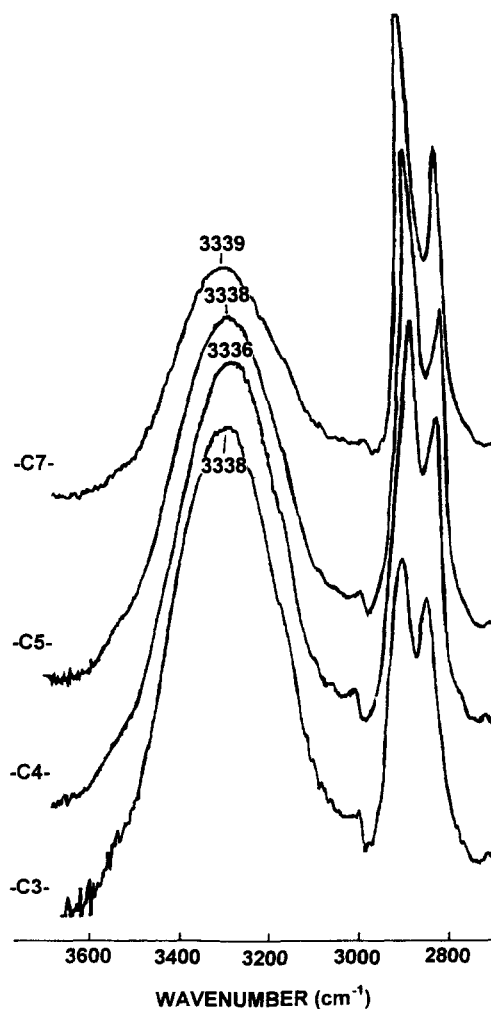


Figure 6 Infra-red spectra of dyes containing -C3-, -C4- and -C7- alkyl spacers

CONCLUSIONS

The interactions of hydroxyl-functionalised dye solute molecules in an amorphous copolyester matrix have been investigated. Simplification of solute structure has allowed i.r. spectroscopy to be a useful tool in determining the nature and extent of different types of solute interactions. Generally, three types of specific solute interactions have been established at various concentrations. There is a dye-polymer intermolecular interaction between the dye hydroxyl group and the polyester carboxyl group, a dye-dye self-association interaction between different dye hydroxyl groups and a dye intramolecular interaction between the hydroxyl group and the tertiary amino group.

The strength of the dye-polymer intermolecular and dye intramolecular interactions is not concentration dependent, whereas the dye-dye self-association interaction is concentration dependent: the higher the concentration the stronger the self-association interaction. The relative proportions of dye-polymer and dye-dye interactions that occur are strongly influenced by the amount of solute present in the polymer. At low solute concentrations the dye-polymer interaction predominates, but as dye concentration increases the dye-dye self-association interaction becomes more favourable.

Dye-dye interactions increase with a greater number of hydroxyl groups. For mono-hydroxyl solutes, the majority of the interactions are dye-polymer in nature, whereas for tri-hydroxyl solutes the dye-dye interaction predominates. Changing the length of the alkyl chain spacer group between the peripheral hydroxyl functionality and the delocalised aromatic core of the dye solute has no discernible effect on the interactions in the range from C₃ to C₇. The strength of all three interactions remains the same, as do the proportions of dye involved in each interaction.

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