Dye–Fiber Interactions in PET Fibers: Hydrogen Bonding Studied by IR-Spectroscopy

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ABSTRACT: Dye–fiber interactions are studied in poly (ethylene terephthalate) fibers by FT-IR spectroscopy. It is shown for the first time that DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) serves as an easy applicable and accurate technique for the study of fibrous structures. This article focuses on the possible hydrogen bond interactions in the dye–fiber system, where the PET fibers are dyed with anthraquinone-based disperse dyes. The dyes and related anthraquinone structures are studied in both the dilute solution state, the solid state, and as present in the PET fibers. It is proven that 1-amino anthraquinones show strong ''chelate-type'' intramolecular hydrogen bonding in all three states. In the fibers an important supplementary intermolecular hydrogen bonding with the C=O groups in the PET fiber is observed. The extend of hydrogen bonding seems to be prone to dye concentration variations. Further analysis by modulated differential scanning calorimetry links the hydrogen bonding to an intrinsic plasticizing effect of the dyes affecting the dye diffusion process. This thus offers a tool for the fundamental understanding of the dyeing process and possible observed differences in dyeing behavior in dye–fiber systems. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1648–1658, 2007

Key words: poly(ethylene terephthalate); fibers; dyes; hydrogen bonding; infrared spectroscopy

INTRODUCTION

With the introduction of ever finer fibers such as microfibers and supermicrofibers in the synthetic fiber market some problems were raised concerning the difficult dyeing behavior of the finer fibers.[1–4] Studies of the color differences between fabrics composed of different fiber fineness revealed that the color differences do not only show up as a difference in color depth, as is generally assumed, but also as a difference in color shade.[5] The observed color differences between the conventional fiber fabric and the microfiber fabric suggest the causes not only to be the different fabric structure but also varying dye–fiber interactions which are a function of dye concentration, dye structure, and fiber morphology. In earlier studies of dye–fiber interactions, the plasticizing effect was revealed of some anthraquinone dyes[6,7] and an interrelation was shown with the diffusion behavior.[8,9] In this article the same fabrics and dyes will be further investigated by infrared spectroscopy as to complement the understanding of the dye–fiber interactions. This article focuses on the possible hydrogen bonding in the dye–fiber system.

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Fibers and fabrics are not suited for conventional FT-IR spectroscopy measurements in transmission, since they do not offer a uniform sample thickness. Therefore, the study of polymers in general is often performed on films, although FT-IR microspectroscopy allows spectral acquisition of small samples and even single fibers. Nevertheless the study of the specific morphology of PET fibers[10–15] with FT-IR spectroscopy is relatively limited, compared with the study of bulk PET (usually prepared as films).[16–25]

The use of IR spectroscopy for the study of interactions between a dye and a polymer has been even less explored. Slark and Hadgett[26] published interactions between dye solutes and polymers, but these are all based on polymer films and the dye is not incorporated into the polymer by a dyeing process but by physical mixing prior to film production. No references have been found in the literature on the study of dye–fiber interactions in PET fibers by FT-IR spectroscopy. This can be understood from the very low concentrations of dye in the fiber that are obtained by a dyeing process, making the subtle variations in the spectrum due to the presence of a dye very difficult to observe. This is especially a problem with fibers, which until relatively recently have been difficult samples to measure in themselves. The limited performed research on dye–fiber interactions so far has been based on indirect evidence. It is how-

ever crucial to study dye–fiber interactions in the fibers directly, as the morphology and interactions may be substantially different from bulk polymer systems.[6,7]

It will be shown in this article that DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) offers a valuable easy applicable technique to study the dye–fiber interactions in fibers. To better understand the hydrogen bonding of the three main anthraquinone dyes studied in the PET fibers, some related model anthraquinone structures will be studied as well. Finally the influence of the dyes on the glass-transition temperature of the fibers will be looked at.

MATERIALS AND METHODS

Materials

A conventional fiber PET fabric and a microfiber PET fabric were used. The single fibers or filaments in the conventional fiber PET fabric have a circular cross-section and a linear density of 5.6 dtex or an approximate diameter of 23–24 μm. The microfiber PET fabric consists of warp fibers with a circular cross-section and weft fibers with a hexagonal cross-section, with a linear density of 0.56 and 0.57 dtex, respectively, or an approximate diameter of 7.5 μm. Further fabric details are given elsewhere.[6]

Three red anthraquinone dyes (AQ1, AQ2, AQ3) and a benzodifuranone dye containing an amino group were supplied by Dystar UK (Cheadle, UK). They were all supplied both as predispersed dye in the powder form and as pure dye. Some related structures to the anthraquinone dyes were investigated as well (Fig. 1) and these were purchased from Aldrich (Steinheim, Germany).

Dyeing experiments

All dyeings were performed in a Mathis Labomat BFA-8 lab dyeing machine, using sealed stainless steel dye pots. The temperature profile applied during the dyeing process is illustrated in Figure 2. An isothermal step of 1 h was used. More details of the dyeing methodology are described elsewhere.[7] After all dyeing processes the standard reduction clearing process was performed and finally the samples were air dried.

To monitor the amount of pure dye absorbed by the fibers, the dye was extracted from the dyed fibers with chloroform using Kumagawa extractors. The concentration of dye was determined with a PerkinElmer Lambda 900 spectrophotometer and by setting up a suitable calibration curve.

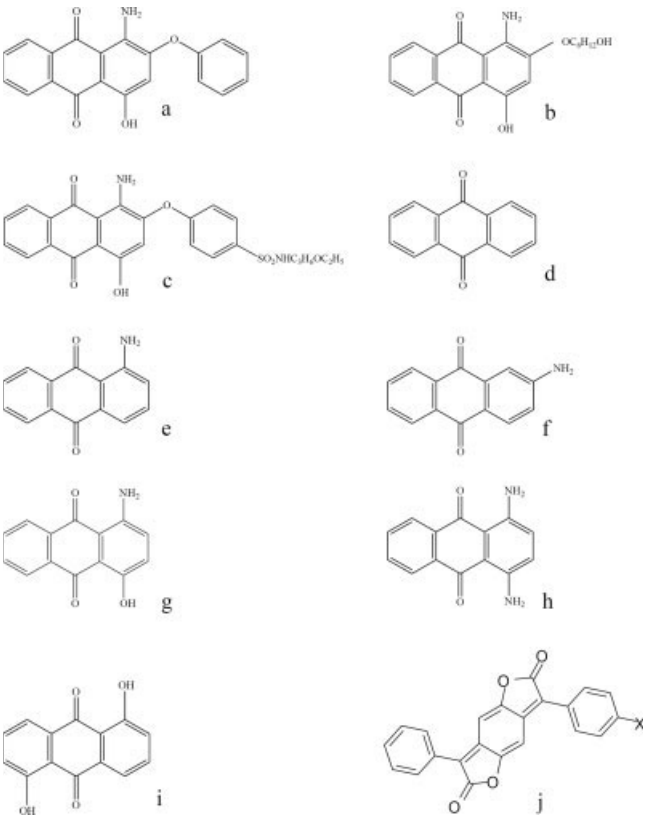

Figure 1 Dye structures. (a) AQ1, (b) AQ2, (c) AQ3, (d) anthraquinone, (e) 1-amino anthraquinone, (f) 2-amino anthraquinone, (g) 1-amino,4-hydroxy anthraquinone, (h) 1,4-diamino anthraquinone, (i) 1,5-dihydroxy anthraquinone, (j) benzodifuranone with X containing an amino group.

FT-IR spectroscopy

Infrared spectra were recorded on a PerkinElmer GX 2000. A Peltier-cooled DTGS Mid-IR detector, a MID-IR source, and an extended KBr beam splitter were used. The spectrometer is also equipped with a PerkinElmer Autoimage microscope to allow micro-spectroscopy measurements. A medium-band MCT detector was used with the microscope. An internal wavelength calibration was performed with a

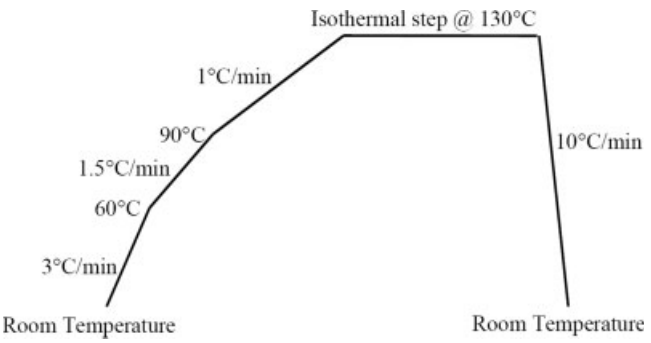

Figure 2 Temperature profile during the dyeing process.

623.99 nm HeNe laser and could be validated with a PerkinElmer validation kit (polystyrene film).

Diffuse reflectance spectra of the PET fabrics were obtained with a PerkinElmer DRIFTS accessory mounted in the main sample compartment. These experiments were performed with 16 scans and a resolution of 4 cm^{-1} in the spectral range 370–4000 cm^{-1} with a data interval of 1 cm^{-1}. A background spectrum was recorded with the provided sandpaper standard samples designed to record a background spectrum with DRIFTS.

Transmission spectra of single fibers were recorded in air by microspectroscopy with a PerkinElmer Autoimage microscope. These experiments were recorded with 256 scans and a resolution of 4 cm^{-1} in the spectral range 580–4000 cm^{-1} with a data interval of 1 cm^{-1}. The aperture size was 12 μm × 80 μm. The background spectrum was recorded in air. The large number of scans was needed due to the very small aperture size, intrinsic to the measurement of fibers. The spectra of the ''pure'' dyes were obtained both as dilute solutions in a nonpolar solvent, $CHCl_3$, or CCl_4 and in the solid state in KBr pellets.

Modulated differential scanning calorimetry

The glass transition of the fibers was monitored by modulated differential scanning calorimetry on a TA Instruments DSC 2920 with MDSC® option using an underlying heating rate of 2°C/min, a 2°C modulation amplitude, and a 60-s modulation period. More details on the methodology are described elsewhere.[6,7]

RESULTS AND DISCUSSION

FT-IR spectroscopy of dyes and related structures

The three standard anthraquinone dyes studied in this work all contain an amino and a hydroxyl group, making them liable to form hydrogen bonds. The IR absorption peaks due to the NH_2 and OH stretching modes are very sensitive to the strength of hydrogen bonding. Both intramolecular and intermolecular dye–dye as well as dye–PET hydrogen bonds may be possible in the dye–fiber system.

In the solid state dye–dye intermolecular hydrogen bonds may be expected between the OH or NH_2 group and the carbonyl oxygen of a neighboring dye molecule.[27,28]

To eliminate intermolecular hydrogen bonds, a spectrum of the dilute dye solution in a nonpolar solvent is taken, which is commonly regarded as a good approximation of a spectrum in the vapor phase, where no intermolecular interactions occur (Fig. 3). Although slight shifts to lower wavenumber

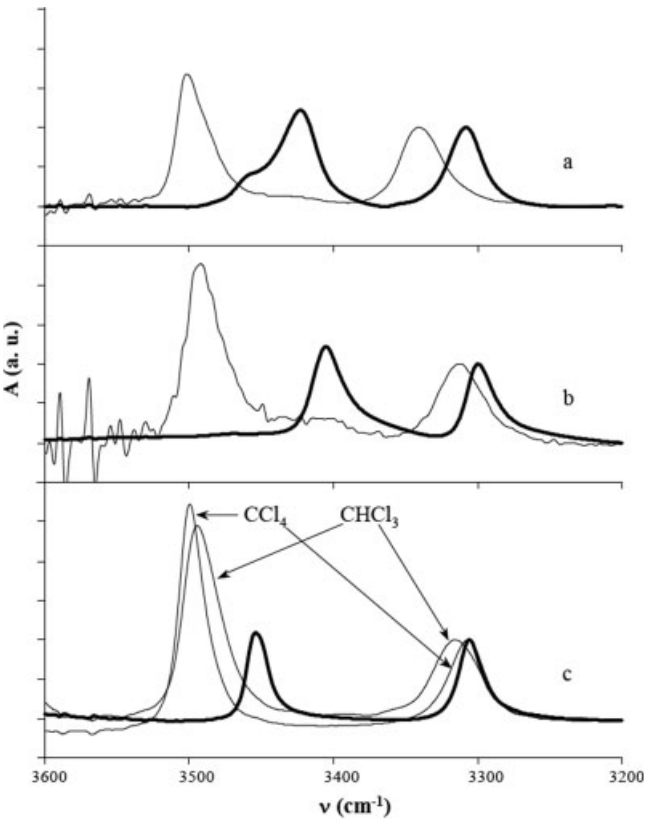

Figure 3 FT-IR spectra of (a) 1-amino anthraquinone, (b) 1-amino, 4-hydroxy anthraquinone, (c) AQ1, (—) dilute solution in $CHCl_3$ (a, b) or $CHCl_3$ and CCl_4 (c), (▬) KBr pellet. All spectra are normalized to an absorbance of 1 at the lowest wavenumber band.

of the OH stretching mode measured in CCl_4 are reported compared to the vapor phase, the peaks are quite characteristic and relatively sharp.[29–31] Not all substances have sufficient solubility in CCl_4 to allow the recording of a quality spectrum. $CHCl_3$ is used instead. The spectrum of AQ1 is however recorded in both CCl_4 and $CHCl_3$ [Fig. 3(c)] and these only show minor differences in peak position and peak ratios, which do not affect the overall conclusions. Therefore, the spectra recorded in $CHCl_3$ of the other substances are regarded as a good approximation of a dilute solution in a nonpolar solvent environment. Unlike intermolecular hydrogen bonding, the intramolecular hydrogen bonding is relatively unaffected by the solute–solvent interaction. Since the amino group is on the 1-position and the hydroxyl group is on the 4-position of the anthraquinone structure, strong intramolecular hydrogen bonds may also be expected with the carbonyl group. Intramolecular hydrogen bonding in 1-substituted anthraquinones, known as ''chelate-type'' hydrogen bonds, has been suggested for both OH, NH_2, and NHR substituents.[32,33] As such the latter may be expected to occur in all studied dyes, both in the solid and the dilute solution state.

Since few references were found for the IR spectra of substituted anthraquinones some simpler substituted anthraquinones related to the dyes were investigated as well. All three dyes (AQ1, AQ2, AQ3) are based on 1-amino, 4-hydroxy anthraquinone and contain a varying substituent in the 2-position. Therefore, anthraquinone, 1-amino anthraquinone, and 1-amino, 4-hydroxy anthraquinone were studied as well (Fig. 3). Anthraquinone itself does not show any significant absorption in this region since it does not contain any hydroxyl or amino groups and is therefore not shown.

All samples show two bands in the spectral region, with the peak position and peak ratio varying according to measurement environment. It is clear that for 1-amino anthraquinone these two bands can be attributed to the antisymmetric (highest wavenumber) and symmetric stretching (lowest wavenumber) modes of the NH_2 group.[29–31]

1-Amino, 4-hydroxy anthraquinone and the AQ1 dye contain both an NH_2 and an OH group. They however also show only two bands. This is due to the very strong intramolecular chelate hydrogen bonding of the OH group, lowering the absorption to 3200–2500 cm^{-1} and making it extremely broad. This renders it sometimes difficult to observe or even ''disappear'' under the C—H stretching modes.[29,31] For amino groups the shifts are usually not that large.[31] The OH band is not visible in the spectra recorded for both states (solid and dilute solution), suggesting the strong intramolecular hydrogen bonding to be present in both extreme states. Thus, the two observed bands may similarly as in 1-amino anthraquinone be attributed to the antisymmetric NH_2 stretching mode and the symmetric NH_2 stretching mode.

To verify the extensive broadening of the OH stretching bands in both above substances, the spectrum of 1,5-dihydroxy anthraquinone was also recorded (not shown here). It indeed gives a very broad band ranging from 3500 cm^{-1} down to 3000 cm^{-1}. When a similar concentration is used as for the amino anthraquinones to record the spectrum, the height of this very broad band is negligible compared to the height of both amino peaks, thus confirming that the OH stretching band may be no longer observable in the spectra of the amino anthraquinones.

Equation (1) shows an empirical relationship between the wavenumbers (ν) of the symmetric and antisymmetric stretching modes for anilines suggested by Krueger.[34]

$$\nu_{sym} = 1023 + 0.682\nu_{antisym} \quad (\nu \text{ in } cm^{-1}) \qquad (1)$$

This equation is valid only for anilines containing two equivalent N—H bonds (i.e. the NH_2 group is free of hydrogen bonding or the two N—H bonds take part in hydrogen bonding in an identical fashion). If the observed wavenumbers do not fit eq. (1), this suggests the two N—H bonds to be differently hydrogen bonded. Equation (1) is set up for anilines and not for substituted anthraquinones, but it may provide a good indication of the equivalence in the hydrogen bonding of both N—H groups for the substances studied here. Table I gives an overview of the measured and calculated, based on eq. (1), wavenumbers for the antisymmetric and symmetric stretching bands. The difference between the measured and calculated value for the antisymmetric band ($\Delta\nu_{antisym}$) provides an indicator for the inequivalence of both N—H bonds.

Table I shows that the difference between the measured and calculated wavenumbers was largest for all substances in the dilute solution state, suggesting that the two N—H bonds of the amino group are less equivalent in a dilute solution in a nonpolar solvent than in the solid state. In addition,

TABLE I
Measured and Calculated Wavenumbers of the Symmetric (ν_{sym}) and Antisymmetric ($\nu_{antisym}$) NH_2 Stretching Modes for the Different Substituted Anthraquinones

Sample		Measured		Calculated	
		ν_{sym} (cm^{-1})	$\nu_{antisym}$ (cm^{-1})	$\nu_{antisym}$ (cm^{-1})	$\Delta\nu_{antisym}$ (cm^{-1})
1-Amino anthraquinone	KBr	3308	3423	3350	73
	$CHCl_3$	3341	3502	3399	103
1-Amino, 4-hydroxy anthraquinone	KBr	3300	3405	3339	66
	$CHCl_3$	3311	3492	3355	137
AQ1	KBr	3306	3454	3348	106
	$CHCl_3$	3316	3494	3362	132
	CCl_4	3307	3499	3349	150
AQ2	KBr	3292	3441	3327	114
	CCl_4	3305	3499	3346	153
AQ3	KBr	3293	3435	3328	107
	$CHCl_3$	3318	3494	3365	129

$\Delta\nu_{antisym}$ is the difference between the measured and calculated value of $\nu_{antisym}$.

the bands in the solid state are shifted towards lower wavenumbers than in dilute solution, showing stronger hydrogen bonding in the solid state than in dilute solution.

Other empirical relationships, similar to eq. (1), are reported by, respectively, Bellamy and Williams[35] and Stewart[36] for primary amines. Similar trends were again observed for both the solid state and dilute solution samples as illustrated in Table I and led to the same conclusions.

Thus a possible hydrogen bonding scheme for the amino group satisfying the above observations is proposed as follows. One N—H bond of the NH_2 group is similar to the OH group being involved in a strong intramolecular hydrogen bonding with the carbonyl group of the anthraquinone structure. This intramolecular hydrogen bonding is present both in the dilute solution state and in the solid state. The second N—H bond is not involved in hydrogen bonding in the dilute solution, resulting in a high inequality between both N—H bonds. In the solid state the second N—H bond is involved in an intermolecular hydrogen bond with a neighbor dye molecule, resulting in a more equivalent hydrogen bonding of both bonds but also lowering the vibration frequencies.

It should further be noted from Figure 3 that the intensity ratio of the antisymmetric NH_2 stretching band relative to the symmetric one is higher for the substituted anthraquinones studied in the dilute solution state than in the solid state. However, no literature references were found to interpret the intensity ratio of both vibration modes.

The suggested intramolecular hydrogen bond of the NH_2 and OH groups with the carbonyl group of the anthraquinone structure should also affect the C=O stretching mode and lower the C=O wavenumber.[37,38] Figure 4 illustrates the C=O stretching vibration band for various anthraquinones measured as a dilute solution in $CHCl_3$.

The only C=O stretching band of anthraquinone is situated at 1676 cm^{-1}, which agrees with the literature value.[38] The bands visible in Figure 4(a) at lower wavenumbers are due to aromatic ring vibrations.[29–31] On the other hand 1-amino anthraquinone [Fig. 4(b)] shows two C=O bands, at 1666 and 1638 cm^{-1}, respectively. The lower frequency spectrum is complicated by the presence of both aromatic ring vibrations and an NH_2 scissoring deformation. 1-Hydroxy anthraquinone is reported to show two C=O bands as well, which are attributed to the free C=O stretching vibration, occurring at 1680–1675 cm^{-1}, and the bonded C=O at 1630–1622 cm^{-1}.[38] In analogy to this the 1666 and 1638 cm^{-1} bands for 1-amino anthraquinone are attributed to, respectively, the free and bonded C=O. This is in agreement with the stated ''chelate-type'' intramolecular hydrogen bonding. 1,5-Dihydroxy anthraquinone [Fig. 4(f)] shows a single band at 1631 cm^{-1}, which again agrees with the literature[38] and is assigned to both bonded carbonyl groups. 1,4-Diamino anthraquinone [Fig. 4(e)] also shows a single band at 1622 cm^{-1}. Similarly 1-amino, 4-hydroxy anthraquinone [Fig. 4(c)], and AQ1 [Fig. 4(d)] only show one band at, respectively, 1622 and 1619 cm^{-1}, which may be attributed to both bonded C=O bonds. It is reported that due to hydrogen bonding, the NH_2 scissoring frequency may coincide with the C=O stretching band,[29] which makes the assignment of the bands visible in Figure 4(b–e) somewhat ambiguous. Nevertheless it is clearly observed that the C=O stretching band is shifted to a lower wavenumber, whether or not it is coinciding with or obscured by other bands. This observation thus confirms that the NH_2 group and the OH group are indeed involved in a strong intramolecular ''chelate-type'' hydrogen bond with the carbonyl group in the anthraquinones studied.

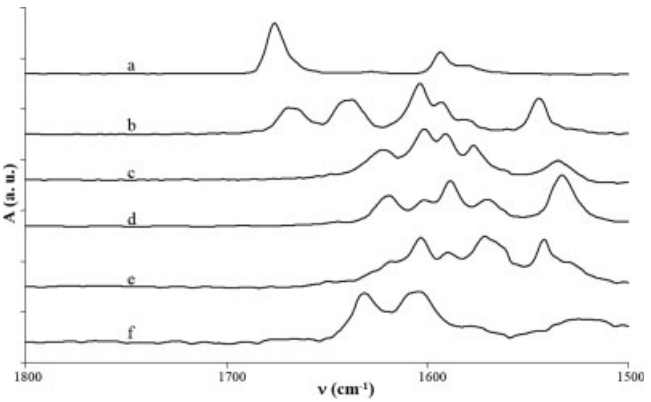

Figure 4 FT-IR spectra of substituted anthraquinones as a dilute solution in $CHCl_3$. (a) Anthraquinone, (b) 1-amino anthraquinone, (c) 1-amino, 4-hydroxy anthraquinone, (d) AQ1, (e) 1,4-diamino anthraquinone, (f) 1,5-dihydroxy anthraquinone. All spectra are normalized to an absorbance of 1 at the wavenumber band of highest intensity.

Figure 5 illustrates the spectra of the AQ2 and AQ3 dyes in the 3700–3100 cm^{-1} wavenumber region for both the solid state and a dilute solution in a nonpolar solvent.

The spectra are more complex but show two major bands similar to the other amino anthraquinones studied. These are again attributed to the antisymmetric and symmetric NH_2 stretching vibrations of the amino group in the 1-position. AQ2 also contains a hydroxyl group at the end of a substituent on the 2-position, whereas AQ3 contains an SO_2NHR group as part of the substituent on the 2-position. This causes some of the observed complexity. Nevertheless the trends in peak positions for both dyes of the two NH_2 stretching bands for both states are similar to the ones observed for the other studied substances

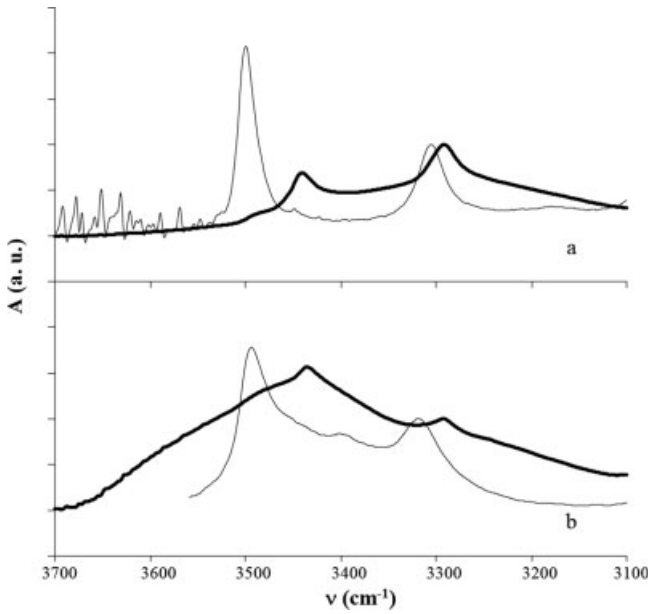

Figure 5 FT-IR spectra of (a) AQ2, (—) dilute solution in CCl_4, (▬) KBr pellet. (b) AQ3, (—) dilute solution in $CHCl_3$, (▬) KBr pellet. All spectra are normalized to an absorbance of 1 at the lowest wavenumber band.

(cf. Table I). For AQ2 the trend in peak intensity ratio is also similar to the other substances, whereas the broad underlying band in the spectrum of AQ3 makes any statement on peak intensity ratio difficult.

The C=O stretching band for both AQ2 and AQ3 in a dilute solution in a nonpolar solvent is similar to AQ1 situated around 1620 cm^{-1}.

The above study generally suggests that the two major peaks observed in the high wavenumber region for the studied amino anthraquinones are due to the antisymmetric and symmetric NH_2 stretching modes. Their relative peak positions and peak intensity ratio are dependent on the state of the substances (dilute solution or solid) recorded, suggesting intramolecular hydrogen bonding in both states and supplementary intermolecular hydrogen bonding in the solid state. The IR absorption of the NH_2 stretching modes of the dyes as present in the fibers can now be compared with these two reference states, which will help to understand the hydrogen bonding in the dye–fiber system.

FT-IR spectroscopy of dyed PET fibers

In this study, FT-IR microspectroscopy and DRIFTS are used to obtain spectra of the fibers. The recording of an IR spectrum of fibers is not as straightforward as for bulk samples that can be transformed in a suitable sample (e.g. thin films). This is due to refraction and reflection at the fiber surfaces, saturation of the more intense peaks for the coarser fibers, and the intrinsic limitations of the finest apertures that may be used in microspectroscopy for the finer fibers.[39,40] Microspectroscopy experiments on the dyed and undyed PET fibers used in this study indeed showed that the spectra of the microfibers were of poor quality due to their intrinsic fineness and could thus not be used. For the conventional fibers, saturation was observed in the 1800–1600 cm^{-1} wavenumber region as expected, but the high wavenumber region of interest here was recorded well.

DRIFTS is a sampling technique developed for the measurement of the diffuse reflectance of powders[41–43] and is not a known technique for the measurement of the diffuse reflectance of fabrics in the MID-IR region. It is important to realize that the theory of Kubelka-Munk for transforming the recorded reflectance data into *K/S* data is based on stringent theoretical conditions, which are not fulfilled in the case of fibers[44,45] but it will be shown here that DRIFTS nevertheless offers a very valuable alternative to FT-IR microspectroscopy for the measurement of fibers. Moreover in the region of interest the results could be confirmed by FT-IR microspectroscopy on the coarser fibers and overall the DRIFTS spectra show a better baseline and less noise than the spectra recorded in transmission, thus resulting in better difference spectra. For this reason the spectra recorded by DRIFTS are preferred in this work, but the DRIFTS spectra as well as the FT-IR microspectroscopy spectra show the same features for both fiber types.

To allow the study of the NH_2 stretching vibrations of a dye within a fiber, spectra are recorded of as received, blank dyed, and dyed fibers. Figure 6 illustrates this for AQ1.

The ''as received'' PET fibers show three weak absorptions in the specified region. Although little is reported on this region in the literature, the peaks around 3630 and 3555 cm^{-1} may be attributed to water present in the polymer. The highest wavenumber band

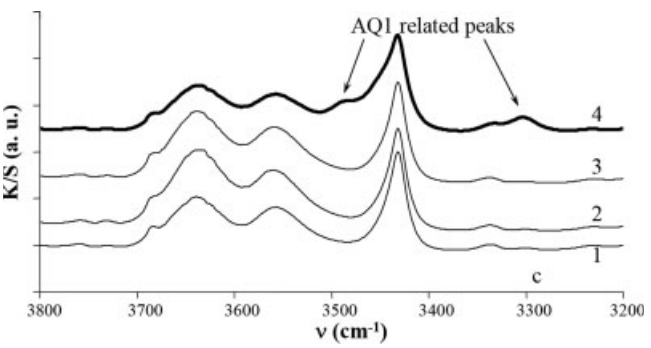

Figure 6 DRIFTS spectra of PET microfibers. All spectra are normalized to a *K/S* value of 1 at the 3430 cm^{-1} PET band. 1: ''as received,'' 2: blank dyed, 3: dyed with pure anthraquinone, 4: dyed with 15% o.w.f. AQ1.

is assigned to free water and the lowest wavenumber band to water bonded to the polymer.[46,47] The peak around 3430 cm^{-1} may be an overtone of the C=O stretching mode at 1719 cm^{-1}.

The blank dyed fibers do not show any important differences in the spectrum compared to the ''as received'' fibers as can be expected. The dyeing with pure anthraquinone does not result in spectral changes either, as indeed it does not contain hydroxyl or amino groups. The dyeing with the AQ1 dye on the other hand results in some additional absorption due to the amino group present.

Hydrogen bonding in the dye–fiber system

Ideally the difference spectrum between the dyed and the blank dyed fibers shows the dye-related bands of a dye molecule in the state it is present in the fiber as well as any variations in the absorption spectrum of the PET due to the dyeing. The absorption peaks of the dye in the fiber are then compared with the absorption peaks of the dye in the solid state and as a dilute solution in a nonpolar solvent.

Difference spectra are calculated for both the conventional fiber and the microfiber fabrics dyed with increasing concentrations of AQ1, AQ2, and AQ3. Also conventional fiber fabrics dyed with 1-amino anthraquinone, 1-amino, 4-hydroxy anthraquinone, and pure dye samples (without dispersing agent) of AQ1, AQ2, and AQ3 are looked at.

Figure 7 shows the high wavenumber region of the difference spectra obtained for the conventional fibers, recorded by FT-IR microspectroscopy compared to the spectra of the substances in the solid state and as a dilute solution in a nonpolar solvent.

It is important to realize that the difference spectra shown in Figure 7 can indeed be regarded as a good approximation of the spectra of the dyes present in the fiber. The PET-related peaks show no major change between the blank dyed and the dyed fibers (cf. Fig. 6 for AQ1) and are thus effectively removed in a difference spectrum. This is true for all dyes tested, except for AQ2. The fabrics dyed with AQ2 show a change in the 3555 cm^{-1} PET band, resulting in an extra peak in the difference spectrum.

1-Amino anthraquinone and 1-amino, 4-hydroxy anthraquinone as present in the fiber show the two NH_2 stretching modes at intermediate wavenumbers compared to the solid state and the dilute solution state [Fig. 7(a,b)]. The intensity ratio of the antisymmetric stretching vibration to the symmetric stretching vibration is also intermediate compared to the two reference states. Further a broadening of the antisymmetric band is observed.

AQ1 shows a similar trend in the intensity ratios of both stretching vibrations. The antisymmetric stretching mode of AQ1 in the fiber is even more broadened compared to the reference states and is extended over almost the total region between the two reference states and even to slightly lower wavenumbers than the solid state. The symmetric stretching mode position varies much less but is also shifted to a slightly lower wavenumber than the solid state.

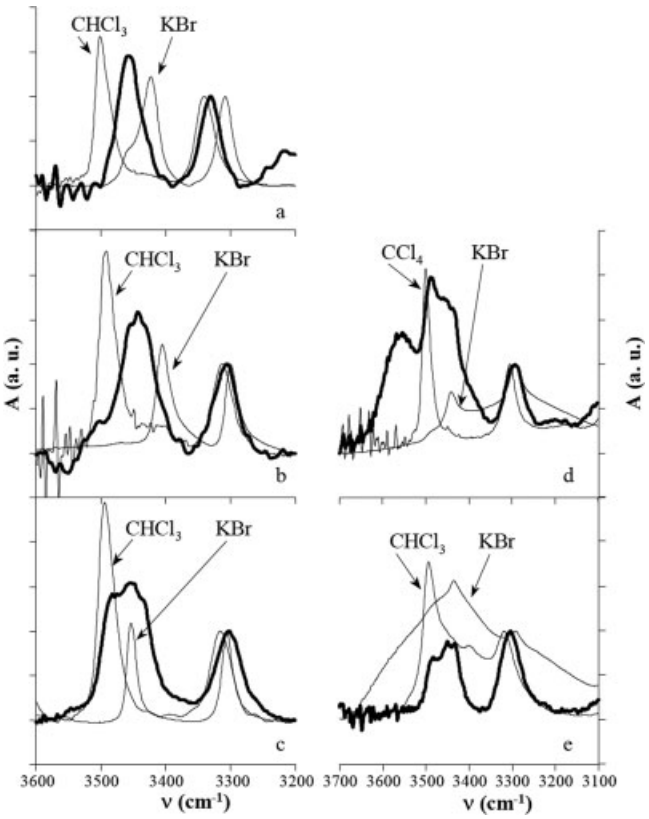

Figure 7 FT-IR spectra of the dyes. (a) 1-Amino anthraquinone, (b) 1-amino, 4-hydroxy anthraquinone, (c) AQ1, (d) AQ2, (e) AQ3. (—) Solid state (KBr) and dilute solution in $CHCl_3$ or CCl_4, (▬) as present in the conventional fiber obtained by a difference spectrum. For (a) and (b) the dyes are applied as pure dye in the dyebath, for (c), (d), and (e) the 15% o.w.f. dye dispersions are used, but when applied as pure dye the spectra are similar except for concentration variations.

The variations in peak intensity ratio of the two NH_2 stretching modes for AQ2 and AQ3 are more difficult to deduce due to overlap with the other bands present in the spectra of AQ2 and AQ3 in the two reference states. On the other hand, the peak positions of the two major bands, which may be attributed to the two NH_2 stretching modes, are again intermediate to those in the two reference states. The difference spectrum of AQ2 shows an extra band at 3555 cm^{-1}. This is due to an increase of this band for the PET fibers after dyeing with AQ2. It may thus probably be attributed to a change in water absorption of the PET fabric after dyeing with AQ2.

TABLE II
Difference between the Measured and Calculated Wavenumber of the Antisymmetric NH_2 Stretching Mode ($\Delta\nu_{antisym}$) for the Solid State, Dilute Solution (in $CHCl_3$, Except AQ2 in CCl_4), and as Present in the Fiber

Sample	$\Delta\nu_{antisym}$ (cm^{-1})		
	Solid	Dilute solution	Fiber
1-Amino anthraquinone	73	103	77
1-Amino, 4-hydroxy anthraquinone	66	137	96
AQ1	106	132	117
AQ2	114	153	141
AQ3	107	129	115

Table II illustrates the difference between the measured and calculated [according to eq. (1)] wavenumber of the antisymmetric band for the anthraquinones in the fiber compared to the reference states. The measured wavenumber of the antisymmetric band for the anthraquinones in the fiber is the mean value at half height. The results show that the inequivalent hydrogen bonding of both N—H bonds of the amino group in the dye–fiber system is intermediate compared to the two reference states.

The data suggest that all anthraquinones examined with an amino group in the 1-position exhibit hydrogen bonding in the fiber different from that found in solid and dilute solution reference states. The dyes may indeed form hydrogen bonds with the C=O groups in the PET polymer. This is confirmed by a slight shift of the C=O band in PET to lower wavenumbers with increasing dye concentration. The intramolecular hydrogen bond of one of both N—H bonds will, however, remain to exist as it is not sensitive to solvent–solute interactions and is regarded to be present in both reference states. One intramolecular hydrogen bond and one dye-PET hydrogen bond will indeed lead to a inequivalence in both bonds intermediate to one intramolecular bond and one free N—H bond in the dilute solution state and one intramolecular and one dye–dye intermolecular hydrogen bond in the solid state.

Further, the broadening and the presence of shoulders of the NH_2 stretching modes in the fiber compared to the reference states suggests the hydrogen bonding in the dye–fiber system to be present in different states.

Figure 8 illustrates the spectra of AQ1 in the 3600 –3200 cm^{-1} wavenumber region as obtained from difference spectra for fabrics dyed with increasing concentrations of dye. For the conventional fibers the spectra were recorded both in transmission by FT-IR microspectroscopy and in diffuse reflection by DRIFTS. Only the DRIFTS spectra are shown as the transmission spectra lead to the same results and conclusions. The spectra are normalized to an absorbance or *K/S* value of one at the lowest wavenumber band to allow the observation of possible differences in relative peak intensity and profile, although of course, both stretching bands are increasing with increasing dye concentration in the original spectra.

Figure 8 illustrates variations in peak intensity ratio of the antisymmetric and symmetric NH_2 stretching modes with dye concentration. The shape of the antisymmetric NH_2 stretching band is slightly affected, suggesting that with increasing dye concentration the type of hydrogen bonding in the dye–fiber system is also slightly altered.

Figure 9 illustrates the spectra for the AQ2 and AQ3 dyes in the 3700–3200 cm^{-1} wavenumber region with increasing concentrations of dye in the dyebath. Again only the spectra obtained by DRIFTS on the conventional fiber fabric are shown, but the FT-IR microspectroscopy experiments on the single conventional fibers as well as the DRIFTS experiments on the microfiber fabrics result in similar spectral trends.

AQ2 shows similar to AQ1 a variation in peak ratio for both NH_2 stretching modes as well as changes in the profile of the antisymmetric stretching band. AQ3 on the other hand shows almost no variations in peak intensity ratio with dye concentration. The more obvious variations in NH_2 stretching bands with dye concentration occurring for AQ2 compared to AQ3 are in agreement with the slightly more

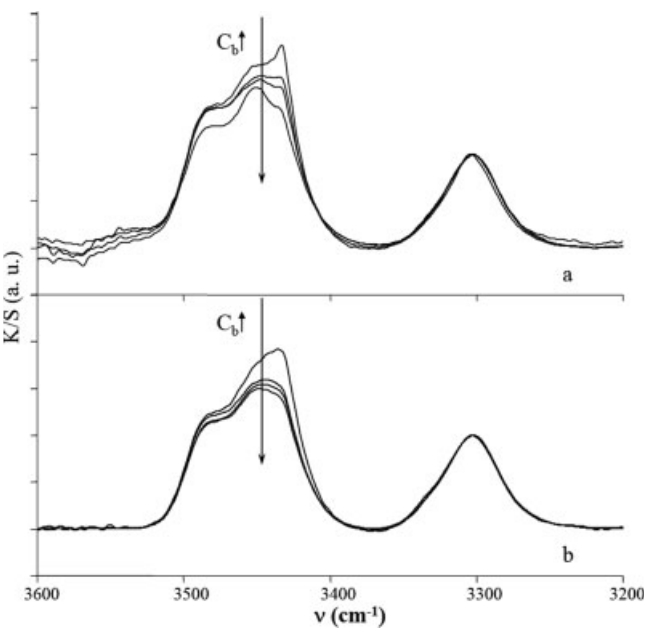

Figure 8 DRIFTS spectra of AQ1 present in the fiber in increasing concentrations (2, 4, 8, and 15% o.w.f. applied dye in the dyebath). All spectra are normalized to a *K/S* value of 1 at the 3302 cm^{-1} wavenumber band. (a) Conventional fiber fabrics. (b) Microfiber fabrics.

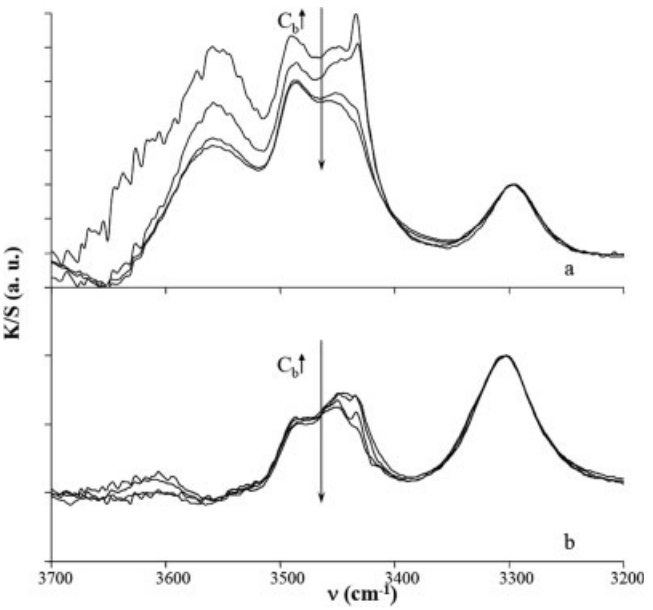

Figure 9 DRIFTS spectra of (a) AQ2 and (b) AQ3 present in the conventional fibers in increasing concentrations (2, 4, 8, and 15% o.w.f. applied dye dispersion in the dyebath). All spectra are normalized to a *K/S* value of 1 at the 3293 cm^{-1} (a) and 3304 cm^{-1} (b) wavenumber band.

obvious shift of the PET C=O peak to lower wavenumber for AQ2.

Thus, although the observed variations with dye concentration are on the limit of the accuracy of the difference spectra, a similar trend was observed for all measurements suggesting some variation in hydrogen bonding in the dye–fiber system with varying dye concentration. To obtain better spectral data of the possible variation in hydrogen bonding with dye concentration, higher dye concentrations would need to be studied. These can however not be obtained on fabrics due to the maximum solubility of the dyes in the fibers.

Relationship between hydrogen bonding and the plasticizing effect of the dyes

To investigate the possible relationship between the hydrogen bonding in the dye–fiber system and the plasticizing effect of the anthraquinone dyes observed in earlier papers,[6,7] the glass-transition temperatures (T_g) of fabrics dyed with various substituted anthraquinones as well as anthraquinone itself were examined. All these anthraquinones are applied to the conventional fiber fabric as pure substances in the dyebath, without any dispersing agent. Table III illustrates the fiber T_g for the fabrics dyed with these anthraquinone structures, as measured by MDSC. The blank dyed fabric and the fabric dyed with 15% o.w.f. AQ1 (applied as dye dispersion) are also shown for comparison. The concentration of pure dye on the fiber (C_f) is given only for some of the substituted anthraquinones as not all of the substituted anthraquinones showed sufficient solubility in chloroform to allow routine determination of the dye concentration. It is however important to realize that the maximum possible amount of pure dye was applied to the fabrics, which could obviously be confirmed by a visual assessment of the color of the dyed fabrics.

Table III shows that the dyeing with anthraquinone itself does not result in a decrease in fiber T_g. A hydroxyl group on the 1 and 5-position does also not result in a plasticizing effect as can be observed for fabrics dyed with 1,5-dihydroxy anthraquinone. An amino group on the 1-position however brings about a decrease in fiber T_g as can be observed for 1-amino anthraquinone, 1-amino, 4-hydroxy anthraquinone, and 1,4-diamino anthraquinone. Thus the plasticizing effect of the AQ1, AQ2, and AQ3 dyes as observed earlier[6,7] is related to the amino group on the 1-position in all of these dyes and not to the hydroxyl group in the 4-position.

These results suggest that the plasticizing effect of these dyes is related to their possibility to form a hydrogen bond with the PET. Indeed anthraquinone itself does not contain any groups possible of forming hydrogen bonds. The hydroxyl groups in all the studied substances are not liable to form hydrogen bonds with the PET, since they will form a strong ''chelate-type'' intramolecular hydrogen bond independent of their environment. On the other hand, the amino group in the 1-position will form a hydrogen bond with the PET, with the concomitant plasticizing effect analogous to the mathematical model proposed by Slark and Hadgett,[48] which stresses the importance of specific dye-polymer interactions with regard to the permeability of a solute in a polymer.

TABLE III
The Fiber T_g (°C) Measured by MDSC on Weft Fibers of the Conventional Fiber Fabric Dyed with Various Substituted Anthraquinones

Sample	T_g (°C)	C_f (mg/g)
Blank dyed	112	–
Anthraquinone	112	–
1,5-Dihydroxy anthraquinone	112	7.7
1-Amino anthraquinone	106	13.9
2-Amino anthraquinone	109	9.9
1-Amino, 4-hydroxy anthraquinone	107	–
AQ1 (pure dye)	107	14.4
15% o.w.f. AQ1 (dye dispersion)	104	33.4
1,4-Diamino anthraquinone	106	–
BzDF containing NH_2	112	–

C_f (mg/g) is the concentration of pure dye on the fiber. Some concentrations could not be measured with the applied methodology.

It should however be noted that an amino group in the 2-position does not result in such a large T_g reduction. This suggests that the plasticizing effect of the anthraquinone dyes studied is not only related to the presence of an amino group, but the position of the amino group also plays an important role with the formation of a strong intramolecular ''chelate-type'' hydrogen bond being significant. It may also be observed from Table III that the dye concentration in the fiber is a little lower for 2-amino anthraquinone than for 1-amino anthraquinone, in agreement with the lower plasticizing effect.

Experiments on fabrics dyed with various concentrations of a benzodifuranone dye containing an amino group also reveal no reduction in fiber T_g. This suggests again the importance of not only the presence of the amino group but also its position in the molecular structure of the dye.

It can therefore be suggested that an interrelation between some specific hydrogen bonding in the dye–fiber system and the plasticizing nature of a dye during the dyeing process exists. As such the nature of the hydrogen bonds will be an important parameter for the dye diffusion process. It may cause a local variation in diffusion coefficient with dye concentration and as such have an ''autocatalytic'' effect.[8,9] FT-IR spectroscopy appears to be a powerful technique permitting a more fundamental understanding of the principles of the dyeing process of PET fibers with disperse dyes.

CONCLUSIONS

Dye–fiber interactions are studied by infrared spectroscopy. It is shown that DRIFTS serves as a good alternative for infrared microspectroscopy for the study of textiles, as microspectroscopy is sometimes not possible due to the inherent fiber-related limitations.

It is proven that 1-amino anthraquinones show strong ''chelate-type'' intramolecular hydrogen bonding in both the diluted state and the solid state. A supplementary intermolecular hydrogen bonding is present in the solid state. In the fiber the 1-amino anthraquinone dyes again show a strong intramolecular hydrogen bonding next to a supplementary intermolecular hydrogen bonding with the C=O groups in the PET fiber.

The hydrogen bonding with the C=O groups in the PET-fiber is related to the intrinsic plasticizing effect of the 1-amino anthraquinones and thus plays an important role in the dye diffusion process. It is also shown that the position of the amino group is of relevance, as in the absence of the strong intramolecular hydrogen bonding the plasticizing effect is far less.

Studying the dye–fiber interactions with increasing dye concentrations revealed slight variations in hydrogen bonding with dye concentration. This may very well lead to the observed color shade differences accompanying the color depth differences.

References

1. Burkinshaw, S. M. Chemical Principles of Synthetic Fibre Dyeing; Chapman & Hall: Glasgow, 1995; Chapter 4.
2. Leadbetter, P.; Dervan, S. J Soc Dyers Colourists 1992, 108, 369.
3. Chao, Y. C.; Chen, S. S. Dyes Pigments 1994, 24, 205.
4. Dupeuble, J.-C. Man-Made Fiber Year Book (Chemiefasern/Textilindustrie) 1991, 88.
5. De Clerck, K.; Rahier, H.; Van Mele, B.; Westbroek, P.; Kiekens, P. To appear.
6. De Clerck, K.; Rahier, H.; Van Mele, B.; Kiekens, P. J Appl Polym Sci 2003, 89, 3840.
7. De Clerck, K.; Rahier, H.; Van Mele, B.; Kiekens, P. J Appl Polym Sci 2003, 90, 105.
8. De Clerck, K.; Van Oostveldt, P.; Rahier, H.; Van Mele, B.; Westbroek, P.; Kiekens, P. Polymer 2004, 45, 4105.
9. De Clerck, K.; Van Oostveldt, P.; Rahier, H.; Van Mele, B.; Westbroek, P.; Kiekens, P. Polymer, 2005, 46, 101.
10. Garton, D. J.; Carlsson, D. J.; Wiles, D. M. Text Res J 1981, 51, 28.
11. Yazdanian, M.; Ward, I. M.; Brody, H. Polymer 1985, 26, 1779.
12. Tungol, M. W.; Bartick, E. G.; Montaser, A. J Forensic Sci 1991, 36, 1027.
13. Carter, R. O.; Carduner, K. R.; Peck, M. C. P.; Motry, D. H. Appl Spectrosc 1989, 43, 791.
14. Chidambaram, D.; Venkatraj, R.; Manisankar, P. J Appl Polym Sci 2003, 89, 1555.
15. Cho, L. L.; Reffner, J. A.; Wetzel, D. L. J Forensic Sci 1999, 44, 283.
16. D'Esposito, L.; Koenig, J. L. J Polym Sci Polym Phys Ed 1976, 14, 1731.
17. Lin, S. B.; Koenig, J. L. J Polym Sci Polym Phys Ed 1983, 21, 2365.
18. Boerio, F. J.; Bahl S. K.; McGraw, G. E. J Polym Sci: Polym Phys Ed 1976, 14, 1029.
19. Hutchinson, J.; Ward, I. M.; Willis, H. A.; Zichy, V. Polymer 1980, 21, 55.
20. Stokr, J.; Schneider, B.; Doskocilova, D.; Lovy, J.; Sedlacek, P. Polymer 1982, 23, 714.
21. Yang, X.; Long, F.; Shen, D.; Qian, R. Polym Commun 1991, 32, 125.
22. Ward, M.; Wilding, M. A. Polymer 1977, 18, 327.
23. Quintanilla, L.; Rodriquez-Cabello, J. C.; Jawhari, T.; Pastor, J. M. Polymer 1993, 34, 3787.
24. Qian, R.; Shen, D.; Sun, F. Macromol Chem Phys 1996, 197, 1485.
25. Pearce, R.; Cole, K. C.; Ajji, A.; Dumoulin, M. M. Polym Eng Sci 1997, 37, 1795.
26. Slark, T.; Hadgett, P. M. Polymer 1999, 40, 1325.
27. Yatsenko, V.; Tafeenko, V. A.; Zakharov, V. N.; Popov, S. I.; Schenk, H. Dyes Pigments 1998, 37, 273.
28. Yatsenko, V.; Chernyshev, V. V.; Popov, S. I.; Sonneveld, E. J.; Schenk, H. Dyes Pigments 2000, 45, 169.
29. Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules. Academic Press: San Diego, 1991; Chapters 4, 10.
30. Smith, B. C. Infrared Spectral Interpretation a Systematic Approach. CRC Press: Boca Raton, 1999; Chapters 3, 5.

31. Bellamy, L. J. The Infrared Spectra of Complex Molecules. Wiley: New York, 1964; Chapters 6, 14.
32. Hallas, G. In Colorants and Auxiliaries: Organic Chemistry and Application Properties, Vol. 1: Colorants; Shore, J., Ed.; Society of Dyers and Colourists: Bradford, 1990; Chapter 6.
33. Yoshida, Z.; Takabayashi, F. Tetrahedron 1968, 24, 913.
34. Krueger, P. J. Nature 1962, 194, 1077.
35. Bellamy, L. J.; Williams, R. L. Spectrochim Acta 1957, 9, 341.
36. Stewart, J. E. J Chem Phys 1959, 30, 1259.
37. Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules; Academic Press: San Diego, 1991; Chapter 9.
38. Bellamy, L. J. The Infrared Spectra of Complex Molecules. Wiley: New York, 1964; Chapter 9.
39. Kirkbride, K. P.; Tungol, M. W. In Forensic Examination of Fibres; Robertson, J., Grieve, M., Eds.; Taylor & Francis: London, 1999; Chapter 8.
40. Lang, P. L.; Richwine, L. J. In Practical Sampling Techniques for Infrared Analysis; Coleman, P. B., Ed.; CRC Press: Boca Raton, 1993; Chapter 6.
41. Culler, S. R. In Practical Sampling Techniques for Infrared Analysis; Coleman, P. B., Ed.; CRC Press: Boca Raton, 1993; Chapter 4.
42. Smith, C. Fundamentals of Fourier Transform Infrared Spectroscopy; CRC Press: New York, 1996; Chapter 4.
43. Kokot, S.; Yang, P.; Gilbert, C. Anal Chim Acta 1996, 332, 105.
44. Kubelka, P.; Munk, F. Zeitschrift für Technische Physik 1931, 12, 593.
45. Kubelka, P. J Opt Soc Am 1948, 38, 448.
46. Sammon, M. C.; Yarwood, J.; Everall, N.; Swart, R.; Hodge, D. J Phys Chem 1998, 102, 3402.
47. Sammon, Y. J.; Everall, N. Polymer 2000, 41, 2521.
48. Slark, T.; Hadgett, P. M. Polymer 1998, 39, 3977.