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Dichroism measurements in forensic fibre examination. Part 4—dyed acrylic and acetate fibres

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ABSTRACT

A number of dyed acrylic and acetate fibre samples were examined with plane polarized light on their dichroic behavior by optical light microscopy (OLM) and microspectrophotometry with plane polarized light (MSP-PPL). It was found that most of these low birefringent fibres possess weak dichroic effects that are very hard to observe with microscopy. However, using MSP-PPL, the linear dichroism could be measured.

A comparison between the dichroic effects found for the same disperse dyes on triacetate (TrAc), diacetate (Ac), polyester (PES) and polyamide (PA) shows that the linear dichroism follows the order: PA>PES >>TrAc, Ac.

1. Introduction

The linear dichroism (LD) is the differential absorption of polarized light with different orientation directions. Three previous publications in this series have dealt with the occurrence of dichroism in polyester fibres [1], in peptidic [2] and in cellulosic [3] fibres.

This work presents the observation and the measurement of linear dichroism in fibre classes possessing low birefringence and will deal with acrylic fibres and cellulose acetates (di- and triacetates). The birefringence (Δn) is the difference between the refractive indices of the two main directions in a fibre : $\Delta n = n(\text{para}) - n(\text{perp})$. Low birefringent fibres have very similar refractive indices in both main fibre directions. This means that light traveling in either direction has almost the same velocity.

Acrylic fibres are man-made aliphatic chains with cyano functional groups pointing in all possible directions. In general, the refractive index along the perpendicular direction is slightly higher than the one along the parallel direction. This results in a low birefringence (with negative elongation) of around -0.003. The homopolymer has a high crystallinity between 65 and 85% and is very difficult to dye. Therefore, copolymers are used which lower the crystallinity and increase the accessibility of dyes in the amorphous zones [4]. In order to increase the tinctorial properties with basic dyes, negatively charged sites are often incorporated (sulphonate groups) and sulfate end groups are also present. For acrylic fibres, the most common dye application classes are basic and disperse dyes.

Acetate fibres are produced by acetylation of the hydroxyl groups in viscose. Almost complete acetylation (ester content of at least 92%) results in triacetate fibres, while diacetate is obtained by subsequent partial hydrolysis. The main difference between diacetate and triacetate is the accessibility of the polymer. The latter fibre subclass is more crystalline and therefore more difficult to dye. The birefringence of acetates is low. For diacetate, slightly positive values of around $+0.003$ are found. For triacetates the birefringence is lower and lies very close to zero. Dyeing of acetates involves mostly the use of disperse dyes, although acid, azoic and ingrain dyes could be applied too.

In this work the linear dichroism of low birefringent fibres (acrylic and acetate fibres) is studied using microscopy and microspectrophotometry with plane polarized light (MSP-PPL). As stated before in Ref. [1] the aims of this work are:

- to explore dichroism in the most common fibre and dye class combinations;
- to examine the relationship between dye structure and the presence or absence of dichroism; and
- to propose a validated and well documented method applicable to forensic fibre examinations.

The same disperse dyes for acetates can also be applied to polyamide and polyester fibres. Therefore, the dichroic effects of a limited amount of disperse dyes on diacetate and triacetate will be

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compared to those found for the same dyes on polyamide and polyester.

2. Experimental

2.1. Acrylics

All samples were obtained from color swatches of dye manufacturers and all are dyed with basic dyes (22 samples) or disperse dyes (18 samples). All samples were dyed with only one dye compound. Undyed samples include polyacrylonitrile homopolymer (PAN) and the main copolymers vinyl acetate (PAN/VA), methyl acrylate (PAN/MA) and methyl methacrylate (PAN/MMA) were obtained from the forensic Fibre Reference Collection of Microtrace.

A list of all acrylic samples is shown in Table 1. The data entered are the sample numbers with reference to our laboratory's fibre reference collection (FRC), the commercial names (uptake of dye in weight percentages), the Colour Index (CI) generic names, CI constitution number and chemical dye class. Most of the dye structures were disclosed and are reported in the Colour Index [5]. For the dyes not mentioned in the Colour Index, information on the chemical dye class was added whenever this could be derived from the spectral band shapes.

2.2. Cellulose acetates

All samples were obtained from color swatches of dye manufacturers and all are dyed with disperse dyes. The 44 triacetate samples (TrAc) and the 20 diacetate samples (Ac) are listed in Table 2. Undyed

Table 1
Dye systems of the acrylic samples, their dichroic features as observed with microscopy and their spectral characteristics (MSP-PPL).

Sample	Ref. FRC	Commercial dye name	Chemical dye class	CI generic name (const. number)	Fibre color	Microscopy	MSP-PPL[d]
PAN1	11941	Astrazon Orange G (4.8%)	Methine	Basic Orange 21 (CI 48035)	Orange	No	$R=1.20$
PAN2	11942	Astrazon Orange 3R (4.2%)	Methine	Basic Orange 21 (CI 48035)	Orange-red	No	$R=1.06$
PAN3	11943	Astrazon Brilliant Red 4G (4.8%)	Cyanine (methine)	Basic Red 14 (CI 48016)	Fuchsia	No	$R=1.17$
PAN4	11944	Astrazon Red 5BL (3.4%)	Azo/monoazo	Basic Red 45	Pink	No	$R=1.04$
PAN5	11945	Astrazon Red GTL (3.2%)	Azo/monoazo	Basic Red 18 (CI 11085)	Salmon	No	$R=1.00$
PAN6	11946	Astrazon Red F3BL (3.4%)	Mixture of 2 monoazo isomers	Basic Red 22 (CI 11055)	Fuchsia	No	$R=1.15$
PAN7	11947	Astrazon Red 6B (4.8%)	Methine	Basic Violet 7 (CI 48020)	Purple	No	$R=1.24$
PAN8	11948	Astrazon Blue 3RL (4.8%)	Anthraquinone	Basic Blue 47 (CI 61111)	Blue	No	$R=1.02; \underline{1.13; 1.12}$
PAN9	11949	Astrazon Blue FGL (6.0%)	Anthraquinone	Basic Blue 22 (CI 61512)	Blue	No	$R=1.00; \underline{1.12; 1.09}$
PAN10	11950	Astrazon Blue FGGL (4.2%)	Azo/monoazo	Basic Blue 41 (CI 11105)	Blue	No	$R=1.13$
PAN11	11951	Astrazon Blue B (3.0%)	Triarylmethane	Basic Blue 5 (CI 42140)	Blue	No	$R=1.07; \underline{1.05}$
PAN12	11952	Astrazon Yellow 5GL 200% (2.0%)	Methine	Basic Yellow 51 (CI 480537)	Yellow	No	$R=1.27$
PAN13	11953	Astrazon Green M (1.2%)	Triarylmethane	Basic Green 4 (CI 42000)	Emerald green	No	$R=1.02; \underline{1.02}$
PAN14	11954	Astrazon Blue BG (4.2%	Oxazine	Basic Blue 3 (CI 51004)	Blue	No	$R=1.18; \underline{1.04}$
PAN15	11955	Astrazon Blue G (3.0%)	Triarylmethane	Basic Blue 1 (CI 42025)	Blue	No	$R=1.09; \underline{1.22}$
PAN16	11956	Astrazon Yellow 8GL (4.5%)	Cyanine (methine)	Basic Yellow 13 (CI 48056)	Yellow	No	$R=1.16$
PAN17	11957	Astrazon Pink FG (5.0%)	Methine	Basic Red 13 (CI 48015)	Pink	No	$R=1.10$
PAN18	11958	Basacryl Yellow 7GL (5.0%)	Methine	Basic Yellow 21 (CI 48060)	Yellow	No	$R=1.04$
PAN19	11959	Basacryl Yellow 5GL (5.0%)	Azo-methine	Basic Yellow 24 (CI 11480)	Yellow	No	$R=1.12$
PAN20	11960	Basacryl Red GL (5.0%)	Azo/monoazo	Basic Red 29 (CI 11460)	Red	No	$R=1.10$
PAN21	11961	Basacryl Blue GL (5.0%)	Azo/monoazo	Basic Blue 54 (CI 11052)	Blue	No	$R=1.15; 1.14$
PAN22	11962	Basacryl Brilliant Red X-4G (6.0%)	Cyanine (methine)	Basic Red 14 (CI 48016)	Red	No	$R=1.09$
PAN23	11963	Dispersol Fast Yellow G (2%)	Azo/monoazo	Disperse Yellow 3 (CI 11855)	Yellow	No	$R=1.15$
PAN24	11964	Dispersol Fast Yellow A (2%)	Nitro	Disperse Yellow 1 (CI 10345)	Yellow	No	$R=1.01$
PAN25	11965	Dispersol Fast Orange B (3.7%)	Azo/monoazo	Disperse Yellow 97 (CI 12055)	Orange	No	$R=1.24$
PAN26	11966	Dispersol Fast Orange Brown RN (2.0%)	Azo/monoazo	Disperse Orange 5 (CI 11100)	Reddish brown	No	$R=1.12$
PAN27	11967	Dispersol Fast Scarlet B (2.0%)	Azo/monoazo	Disperse Red 1 (CI 11110)	Pink	No	$R=1.10$
PAN28	11968	Dispersol Fast Crimson B (2.0%)	Azo/monoazo	Disperse Red 13 (CI 11115)	Pink	No	$R=1.04$
PAN29	11969	Duranol Red 2B (2.0%)	Anthraquinone	Disperse Red 15 (CI 60710)	Pink	No	$R=1.19; 1;19$
PAN30	11970	Duranol Red X3B (2.0%)	Anthraquinone	Disperse Red 11 (CI 62015)	Pink	No	$R=1.35; 1.36$
PAN31	11971	Duranol Violet 2R (1.5%)	Anthraquinone	Disperse Violet 1 (CI 61100)	Reddish violet	No	$R=1.14; 1.14$
PAN32	11972	Duranol Brilliant Violet BR (2.0%)	Anthraquinone	Disperse Violet 8 (CI 62030)	Bluish violet	No	$R=1.16; 1.16$
PAN33	11973	Duranol Brilliant Blue CB (0.75%)	Anthraquinone	Disperse Blue 1 (CI 64500)	Blue	No	$R=1.07; 1.06$
PAN34	11974	Duranol Blue Green B (0.3%)	Anthraquinone	Disperse Blue 7 (CI 62500)	Blue	No	$R=1.16; 1.16$
PAN35	11975	Dispersol Fast Orange G (0.4%)	Azo[e]		Orange	No	$R=1.10$
PAN36	11976	Dispersol Fast Yellow GR (3.0%)			Yellow	No	$R=\underline{0.97}; 1.06$
PAN37	11977	Dispersol Violet RN (1.5%)	Anthraquinone[e]		Violet	No	$R=1.15; 1.15$
PAN38	11978	Duranol Blue G (3.0%)	Anthraquinone[e]		Blue	No	$R=1.18; 1.18$
PAN39	11979	Duranol Blue GN (3.0%)	Anthraquinone[e]		Blue	No	$R=1.13; 1.13$
PAN40	11980	Duranol Grey TN (3.0%)			Grey	No	$R=\underline{1.11}; 1.24; \underline{1.26}; 1.26$
PAN41	44	Undyed acrylic (PAN/VA)[a]					
PAN42	41	Undyed acrylic (PAN/MA)[b]					
PAN43	13	Undyed acrylic (PAN/MMA)[c]					

The Astrazon and Basacryl dye series are basic dyestuffs from Bayer and BASF respectively.
The Dispersol and Duranol dye series are all disperse dyes from ICI.

[a] Acrilan® S16 sample from the Microtrace Fibre Reference Collection (manufacturer Solutia).
[b] Velicren® sample from the Microtrace Fibre Reference Collection (manufacturer Snia).
[c] Creslan® T61GS sample from the Microtrace Fibre Reference Collection (manufacturer Cyanamid).
[d] Effects relating to the main absorption bands are underlined.
[e] Most probable dye class, derived from the spectral band shapes.

Table 2

Disperse dye systems of the triacetate (TrAc) and diacetate (Ac) samples, their dichroic features as observed with microscopy and their spectral characteristics (MSP-PPL) and comparison with polyester (PES), polyamide (PA) samples. Data from previous work [1] are reported in italic font.

Sample	FRC	Commercial name	Chemical dye class	CI generic name (const. number)	Fibre color	Microscopy	MSP-PPL[c]
TrAc1	11623	Resolin Yellow GGLS (6.0%)	Nitro	Disperse Yellow 42 (CI 10338)	Yellow	No	$R = 1.29$
PES79	*1513*	*Foron Yellow SE-FL*		*Disperse Yellow 42 (CI 10338)*	*Bright yellow*	*No*	$R = \underline{1.24}$
TrAc2	11624	Resolin Yellow RL (3.0%)	Azo/monoazo	Disperse Yellow 60 (CI 12712)	Yellow	No	$R = \overline{1.20}\ \Delta\lambda = +5$ nm
PES84	*11553*	*Resolin Yellow RL (5.0%)*		*Disperse Yellow 60 (CI 12712)*	*Yellow*	*Strong*	$R = 2.04\ \Delta\lambda = +25$ *nm*
TrAc3	11625	Resolin Orange 3GL (3.6%)	Azo/disazo	Disperse Orange 66	Yellow	Weak	$R = 1.31\ \Delta\lambda = +15$ nm
TrAc4	11627	Resolin Yellow Brown 3GL (3.0%)	Azo/disazo	Disperse Orange 29 (CI 26077)	Orange	Weak	$R = 1.21\ \Delta\lambda = +10$ nm
TrAc5	11628	Resolin Scarlet 3GL (3.0%)	Azo/monoazo	Disperse Red 106 (CI 11131)	Orange	No	$R = 1.28$
PES85	*11554*	*Resolin Scarlet 3GL (5.0%)*		*Disperse Red 106 (CI 11131)*	*Orange*	*Strong (orange-brown>orange)*	$R = 1.90\ \Delta\lambda = +5$ *nm*
TrAc6	11629	Resolin Scarlet RR (3.0%)	Azo/monoazo	Disperse Red 50 (CI 11226)	Orange	No	$R = 1.15\ \Delta\lambda = +10$ nm
TrAc7	11630	Resolin Red GR (3.0%)	Azo/monoazo	Disperse Red 65 (CI 11228)	Red	Weak	$R = 1.27\ \Delta\lambda = +5$ nm
TrAc8	11631	Resolin Red FB (3.0%)	Anthraquinone	Disperse Red 60 (CI 60756)	Pink	Weak	$R = 1.35; 1.40$
PES70	*1560*	*Foron Brilliant Red E-2BL*		*Disperse Red 60 (CI 60756)*	*Bright red*	*Weak*	$R > 1.3$[d]
TrAc9	11632	Resolin Brilliant Red BLS (6.0%)	Anthraquinone	Disperse Red 159	Red	No	$R = 1.26; 1.28$
TrAc10	11633	Resolin Red BRL (3.0%)	Azo/monoazo	Disperse Red 134	Red	Weak	$R = 1.36$
TrAc11	11634	Resolin Red FRL (3.0%)	Azo/monoazo	Disperse Red 177 (CI 11122)	Red	No	$R = 1.17$
PES72	*2914*	*Intrasil Red H-FTS*		*Disperse Red 177 (CI 11122)*	*Red*	*Strong*	$R = 1.90$
TrAc12	11635	Resolin Red BBL (3%)	Azo/monoazo	Disperse Red 82 (CI 11140)	Red	Weak	$R = 1.35$
TrAc13	11636	Resolin Rubin BL (3.0%)	Azo/monoazo	Disperse Violet 40 (CI 11218)	Red	No	$R = 1.32$
PES88	*11557*	*Resolin Rubin BL (5.0%)*		*Disperse Violet 40 (CI 11218)*	*Red*	*Strong (dark red>red)*	$R > 1.5$[d]
TrAc14	11637	Resolin Red Violet FBL (3.0%)	Anthraquinone	Disperse Violet 26 (CI 62025)	Purple	No	$R = 1.23; 1.24$
PES89	*11558*	*Resolin Red Violet FBL (5.0%)*		*Disperse Violet 26 (CI 62025)*	*Purple*	*Strong*	$R = 2.02; 2.01$
TrAc15	11638	Resolin Violet RL (3.0%)	Anthraquinone	Disperse Violet 28 (CI 61102)	Grey	Weak	$R = 1.20; 1.20$
PES90	*11559*	*Resolin Violet RL (5.0%)*		*Disperse Violet 28 (CI 61102)*	*Purple*	*Strong*	$R = 1.79; 1.82$
TrAc16	11639	Resolin Blue 3 RLS (3.0%)	Azo/monoazo	Disperse Blue 287 (CI 112025)	Blue	Weak	$R = 1.34$
TrAc17	11640	Resolin Blue FR (4.0%)	Anthraquinone	Disperse Blue 154	Blue	No	$R = 1.22$
TrAc18	11641	Resolin Blue FBL (3.0%)	Anthraquinone	Disperse Blue 56 (CI 63285)	Blue	No	$R = 1.22; 1.22$
PES60	*11547*	*Palanil Blue R (1.5%)*		*Disperse Blue 56 (CI 63285)*	*Blue*	*Strong*	$R = 2.46; 2.37$
TrAc19	11642	Resolin Blue BBLSN (3.0%)	Azo/monoazo (2 compound mixture)	Disperse Blue 165:2 (CI 111420)	Blue	Weak	$R = 1.23; 1.17$
TrAc20	11643	Resolin Blue BBLS (1.8%)	Azo/monoazo	Disperse Blue 165 (CI 11077)	Blue	Weak	$R = 1.20; 1.17$
TrAc21	11644	Resolin Blue BSL (3.0%)	Anthraquinone (2 compound mixture)	Disperse Blue 73 (CI 63265)	Blue	Weak	$R = 1.34; 1.34$
PES65	*1473*	*Foron Blue S-BGL*		*Disperse Blue 73 (CI 63265)*	*Bright blue*	*Strong*	$R > 1.8; 1.5$[d]
TrAc22	11645	Celliton Scarlet B (2.0%)	Azo/monoazo	Disperse Red 1 (CI 11110)	Orange	No	$R = 1.24$
Ac1	11646	Celliton Scarlet B (2.0%)		Disperse Red 1 (CI 11110)	Orange	No	$R = 1.18$
PAN27	11967	Dispersol Fast Scarlet B (2.0%)		Disperse Red 1 (CI 11110)	Pink	No	$R = 1.10$
PES11	*11498*	*Dispersol Fast Scarlet B (4.0%)*		*Disperse Red 1 (CI 11110)*	*Pale orange*	*Strong*	$R = 1.92$
TrAc23	11647	Samaron Yellow H3GL (1.5%)	Quinoline	Disperse Yellow 64 (CI 47023)	Yellow	No	$R = 1.26; \underline{1.26}$
Ac2	11648	Samaron Yellow H3GL (1.5%)		Disperse Yellow 64 (CI 47023)	Faint yellow	No	$R = 1.21; \underline{1.20}$
PA110	11649	Samaron Yellow H3GL (1.5%)		Disperse Yellow 64 (CI 47023)	Yellow	Strong	$R = 2.44; \underline{2.50}$
PES121	11650	Samaron Yellow H3GL (1.5%)		Disperse Yellow 64 (CI 47023)	Yellow	Strong	$R = 1.85; \underline{1.97}$
TrAc24	11651	Samaron Orange HFFG	Aminoketone	Disperse Orange 32 (CI 562475)	Yellow	No	$R = 1.52$
PES122	11652	Samaron Orange HFFG (3.0%)		Disperse Orange 32 (CI 562475)	Yellow	Strong	$R = 1.74$
TrAc25	11653	Samaron Brilliant Orange H4R	Azo/monoazo	Disperse Orange 42	Orange	No	$R = 1.20; 1.21$
PES123	11654	Samaron Brilliant Orange H4R (2.0%)		Disperse Orange 42	Orange	Strong	$R = 1.22; 1.23$
TrAc26	11655	Samaron Pink FRL (1.5%)	Anthraquinone	Disperse Red 91 (CI 60753)	Pink	Weak	$R = 1.40; 1.38$
Ac3	11656	Samaron Pink FRL (1.5%)		Disperse Red 91 (CI 60753)	Pink	No	$R = 1.38; 1.39$
PA111	11657	Samaron Pink FRL (1.5%)		Disperse Red 91 (CI 60753)	Pink	Strong	$R = 2.84; 2.90$
PES124	11658	Samaron Pink FRL (1.5%)		Disperse Red 91 (CI 60753)	Pink	Strong	$R = 2.44; 2.51$
TrAc27	11659	Samaron Red HBL (1.5%)	Azo/monoazo	Disperse Red 73 (CI 11116)	Red	Strong	$R = 1.35$
Ac4	11660	Samaron Red HBL (1.5%)		Disperse Red 73 (CI 11116)	Red	Weak	$R = 1.21$
PES125	11661	Samaron Red HBL (2.0%)		Disperse Red 73 (CI 11116)	Red	Strong	$R = 2.15$
TrAc28	11662	Samaron Violet HFRL (1.5%)	Anthraquinone	Disperse Violet 26 (CI 62025)	Purple	Weak	$R = 1.47; 1.47$
PES126	11663	Samaron Violet HFRL (4.0%)		Disperse Violet 26 (CI 62025)	Purple	Strong	$R = 1.66; 1.68$
TrAc29	11664	Samaron Orange HB (1.5%)	Azo[e]		Yellow	No	$R = 1.31$
Ac5	11665	Samaron Orange HB (1.5%)			Yellow	No	$R = 1.60\ \Delta\lambda = +5$ nm
PA112	11666	Samaron Orange HB (1.5%)			Yellow	Strong	$R = 1.93\ \Delta\lambda = +5$ nm
PES127	11667	Samaron Orange HB (2.5%)			Yellow	Strong	$R = 1.60$
TrAc30	11668	Samaron Orange HRRE (1.5%)	Azo[e]		Orange	Weak	$R = 1.41\ \Delta\lambda = +5$ nm
Ac6	11669	Samaron Orange HRRE (1.5%)			Orange	No	$R = 1.21$
PA113	11670	Samaron Orange HRRE (1.5%)			Orange	Strong	$R = 1.48\ \Delta\lambda = +10$ nm
PES128	11671	Samaron Orange HRRE (3.0%)			Orange	Strong	$R = 1.51\ \Delta\lambda = +5$ nm
TrAc31	11672	Samaron Red GL (1.5%)	Azo[e]		Red	Weak	$R = 1.19$
Ac7	11673	Samaron Red GL (1.5%)			Red	No	$R = 1.31$
PES129	11674	Samaron Red GL (2.5%)			Red	Strong	$R = 1.72\ \Delta\lambda = +5$ nm
TrAc32	11675	Samaron Red RL (1.5%)	Azo[e]		Red	Weak	$R = 1.29$

(continued on next page)

Table 2 (*continued*)

Sample	FRC	Commercial name	Chemical dye class	CI generic name (const. number)	Fibre color	Microscopy	MSP-PPL[c]
Ac8	11676	Samaron Red RL (1.5%)			Red	Weak	$R = 1.35$
PES130	11677	Samaron Red RL (2.0%)			Red	Strong	$R = 1.72$
TrAc33	11678	Samaron Blue FBL (1.5%)	Anthraquinone[e]		Blue	No	$R = 1.26;\ 1.26$
Ac9	11679	Samaron Blue FBL (1.5%)			Blue	No	$R = 1.12;\ 1.17$
PA114	11680	Samaron Blue FBL (1.5%)			Blue	Strong	$R = 2.37;\ 2.33$
PES131	11681	Samaron Blue FBL (2.0%)			Blue	Strong	$R = 1.91;\ 1.86$
TrAc34	11682	Samaron Blue H3R (1.5%)	Anthraquinone[e]		Blue	No	$R = 1.23;\ 1.23$
Ac10	11683	Samaron Blue H3R (1.5%)			Grey	No	$R = 1.19;\ 1.18$
PA115	11684	Samaron Blue H3R (1.5%)			Blue	Strong	$R = 1.81;\ 1.83$
PES132	11685	Samaron Blue H3R (3.0%)			Blue	Strong	$R = 1.42;\ 1.42$
TrAc35	11686	Samaron Blue TR (1.5%)			Blue	No	$R = 1.30;\ 1.29$
Ac11	11687	Samaron Blue TR (1.5%)			Blue	No	$R = 1.17;\ 1.18$
PA116	11688	Samaron Blue TR (1.5%)			Blue	Strong	$R = 1.74$ $\Delta\lambda = -10$ nm
PES133	11689	Samaron Blue TR (1.5%)			Blue	Strong	$R = 1.55;\ 1.46$
TrAc36	11690	Samaron Brown HR (1.5%)	Azo[e]		Orange	Weak	$R = 1.35$
Ac12	11691	Samaron Brown HR (1.5%)			Orange	No	$R = 1.27$
PA117	11692	Samaron Brown HR (1.5%)			Orange	Strong	$R = 1.47$ $\Delta\lambda = +15$ nm
TrAc37	11693	Samaron Brown HRN (1.5%)	Azo/monoazo	Disperse Brown 1 (CI 11152)	Orange	Weak	$R = 1.23$
Ac13	11694	Samaron Brown HRN (1.5%)		Disperse Brown 1 (CI 11152)	Orange	Weak	$R = 1.32$
PA118	11695	Samaron Brown HRN (1.5%)		Disperse Brown 1 (CI 11152)	Red	Weak	$R > 1.1$[d]
PES134	11696	Samaron Brown HRN (1.5%)		Disperse Brown 1 (CI 11152)	Orange	Strong	$R = 1.79$ $\Delta\lambda = +10$ nm
TrAc38	11697	Celliton Fast Rubine 3B (2.0%)	Azo[e]		Red	Weak	$R = 1.25$
Ac14	11698	Celliton Fast Rubine 3B (2.0%)			Red	No	$R = 1.24$
TrAc39	11699	Celliton Fast Violet 6B (2.5%)	Anthraquinone[e]		Purple	No	$R = 1.16;\ 1.21$
Ac15	11700	Celliton Fast Violet 6B (2.5%)			Purple	No	$R = 1.21;\ 1.20$
TrAc40	11701	Celliton Fast Blue FFR (2.0%)	Anthraquinone[e]		Blue	No	$R = 1.21;\ 1.20$
Ac16	11702	Celliton Fast Blue FFR (2.0%)			Blue	No	$R = 1.14;\ 1.10$
TrAc41	11703	Celliton Fast Green 3BS (8.0%)	Anthraquinone[e]		Blue	No	$R = 1.42;\ \underline{1.39}$
Ac17	11704	Celliton Fast Green 3BS (8.0%)			Blue	No	$R = 1.22;\ \underline{1.20}$
TrAc42	11705	Celliton Fast Dark Green B (4.0%)			Grey	No	$R = 1.22;\ \underline{1.11}$
Ac18	11706	Celliton Fast Dark Green B (4.0%)			Green	No	$R = 1.15;\ \underline{1.14;\ 1.11}$
TrAc43	11707	Celliton Brilliant Green 3G (3.0%)			Green	No	$R = \underline{1.16};\ 1.20;\ 1.18;\ 1.17$
Ac19	11708	Celliton Brilliant Green 3G (3.0%)			Green	No	$R = \underline{1.13};\ 1.17;\ 1.16;\ 1.12$
TrAc44	11709	Celliton Fast Green FFG (3.0%)			Green	No	$R = \underline{1.23};\ 1.20;\ 1.20;\ 1.20$
Ac20	11710	Celliton Fast Green FFG (3.0%)			Green	No	$R = \underline{1.20};\ 1.12;\ 1.12;\ 1.12$
TrAc45	2	Undyed triacetate[a]					
Ac21	3	Undyed diacetate[b]					

The Resolin (Bayer), Celliton (BASF), and Samaron (Cassella) dye series are disperse dyestuffs.

[a] Arnel® sample from the Microtrace fibre reference collection (manufacturer Celanese).

[b] Estron® sample from the Microtrace fibre reference collection (manufacturer Eastman Fibers).

[c] Effects relating to the main absorption bands are underlined.

[d] Saturation effect.

[e] Most probable dye class, derived from the spectral band shapes.

samples of both acetates were obtained from the forensic fiber reference collection of Microtrace.

2.3. Other samples

A selection of polyamide (PA) and polyester (PES) samples was made. These comprise samples which were dyed with the same disperse dyes as for the cellulose acetate samples and these are listed in Table 2. Moreover, a number of previously studied polyester, samples were added and these are marked in italic font.

2.4. Microscopy

All samples were examined with microscopy under plane polarized light using the same methodology as the one previously described [1].

The fibre color as observed in bright field and the color description using polarized light of both principal directions can be found respectively in the third last and second last column of Tables 1 and 2.

2.5. Microspectrophotometry

All samples have been measured with MSP-PPL, using exactly the same methodology as the one previously described [1]. However, as a small dichroic effect is expected for low birefringent fibres, the absorption spectra were obtained using 10 accumulations of 500 ms instead of the standard settings (5 accumulations, integration time of 350 ms).

A careful choice of the measurement position was made. For the crenate cross section of acetate fibres and for acrylic fibres possessing a bean or dogbone cross section the recommendations of the European Fibres Group (EFG) [6] were followed.

The spectral characteristics (dichroic ratio, R and band shifts, $\Delta\lambda$) of the samples as obtained using MSP-PPL are summarized in the last column of Tables 1 and 2.

3. Results

3.1. Undyed samples

No absorption effects were observed for undyed acrylics and acetates.

3.2. Acrylic samples

All 40 dyed samples were observed with microscopy in bright field and with one polarizer inserted, with the fibre oriented consecutively in a parallel and in a perpendicular position with respect to the polarization direction. The observations of the fibre color and the dichroic effects of these samples are listed in Table 1.

None of the samples show any observable dichroic effects using microscopy. The absorption spectra obtained using MSP-PPL show that the effects on acrylics are indeed weak. No band shifts are observed; only weak intensity changes are noted. The highest dichroic ratio calculated from the spectra of basic dyes is 1.25 and the highest shift in any of the complementary chromaticity coordinates is about $\delta = 0.015$. For the spectra of disperse dyes on the acrylic fibres, the highest dichroic ratio found is 1.35 and $\delta = 0.030$. An illustration of this very weak linear dichroism for a triarylmethane dye is given in Fig. 1. No changes are observed with microscopy. Using MSP-PPL, a maximum of only 0.06 AU is found in the LD-spectrum.

3.3. Acetate samples

The disperse dyed diacetate and triacetate samples all show a weak positive dichroism which is generally somewhat higher than the effects found in acrylics. The highest dichroic ratio found in acetates is 1.60.

With microscopy, in 19 of the 44 triacetate samples a weak dichroism was observed, in one sample a strong effect was noted and 24 samples showed no noticeable effect.

For diacetate, only 3 out of 20 samples were described as having a weak dichroism while for the remaining samples no effect was observed.

The dichroic ratio of absorption bands found in 20 samples of di- and triacetates dyed with the same disperse dye compounds is represented in Fig. 2. Although the majority of the triacetates seem to possess a slightly higher dichroic effect, no good correlation was found.

3.4. Comparison between disperse dyed samples

Several samples have been examined which have been dyed with the same disperse dyes on different substrates, allowing for direct comparison of the spectral data for the acetates with those obtained for polyamide and polyester.

An example is given for triacetate and diacetate fibres (Fig. 3) and to polyamide and polyester (Fig. 4) dyed with Samaron Blue H3R. The dichroic behavior of the samples is quite different. The cellulose acetate fibres both have low and comparable dichroic ratios, while the polyester and polyamide fibres show a much larger effect.

The dichroic ratio of absorption bands found in the acetate and the polyamide samples has been plotted against those found for polyesters dyed with the same disperse dye compounds. For some absorption bands saturation effects were noted and these dichroic ratios have not been taken into account. The relationships are represented in Fig. 5. Although no good correlation was found

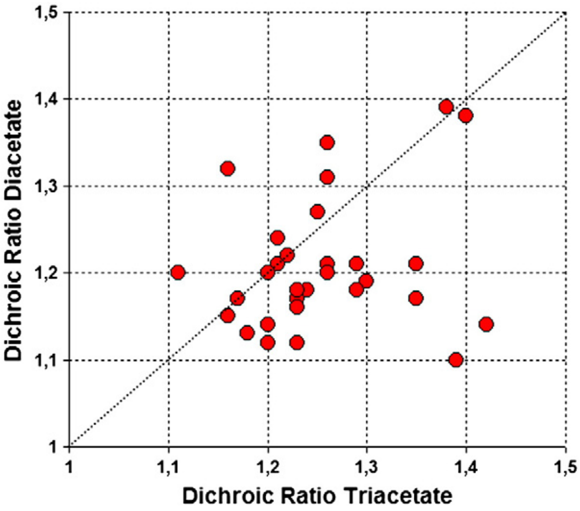

Fig. 2. Scatterplot of the dichroic ratio calculated for the absorption bands of 20 disperse dyes on triacetates and diacetates. The dotted line represents equal dichroic effects.

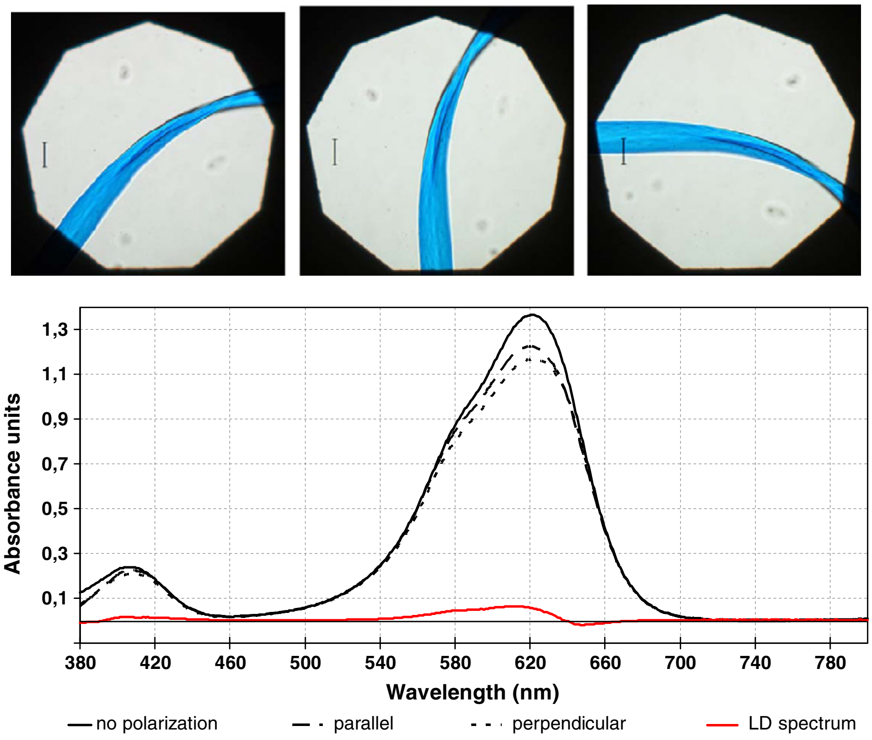

Fig. 1. Above: microscopic observation of a dogbone shaped acrylic fibre dyed with Basic Blue 5 (PAN11) in bright field (left) and with polarized light oriented respectively parallel with (middle) and perpendicular to (right) the fibre's axis. Below: the corresponding absorption spectra in the parallel and the perpendicular position. The resulting LD spectrum has very low values over the whole range.

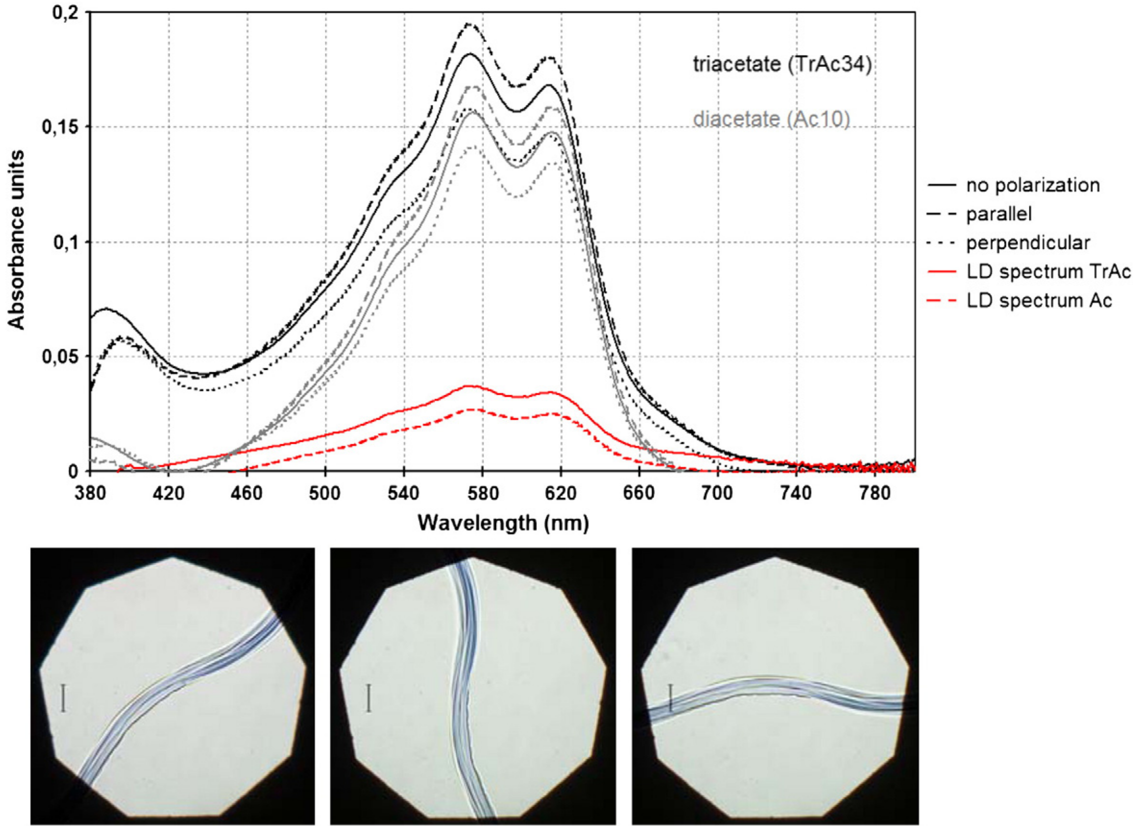

Fig. 3. Above: MSP-PPL spectra of triacetate and diacetate dyed with the disperse dye Samaron Blue H3R.Below: microscopic observation of the diacetate sample in bright field (left) and with polarized light oriented respectively parallel with (middle) and perpendicular to (right) the fibre's axis.

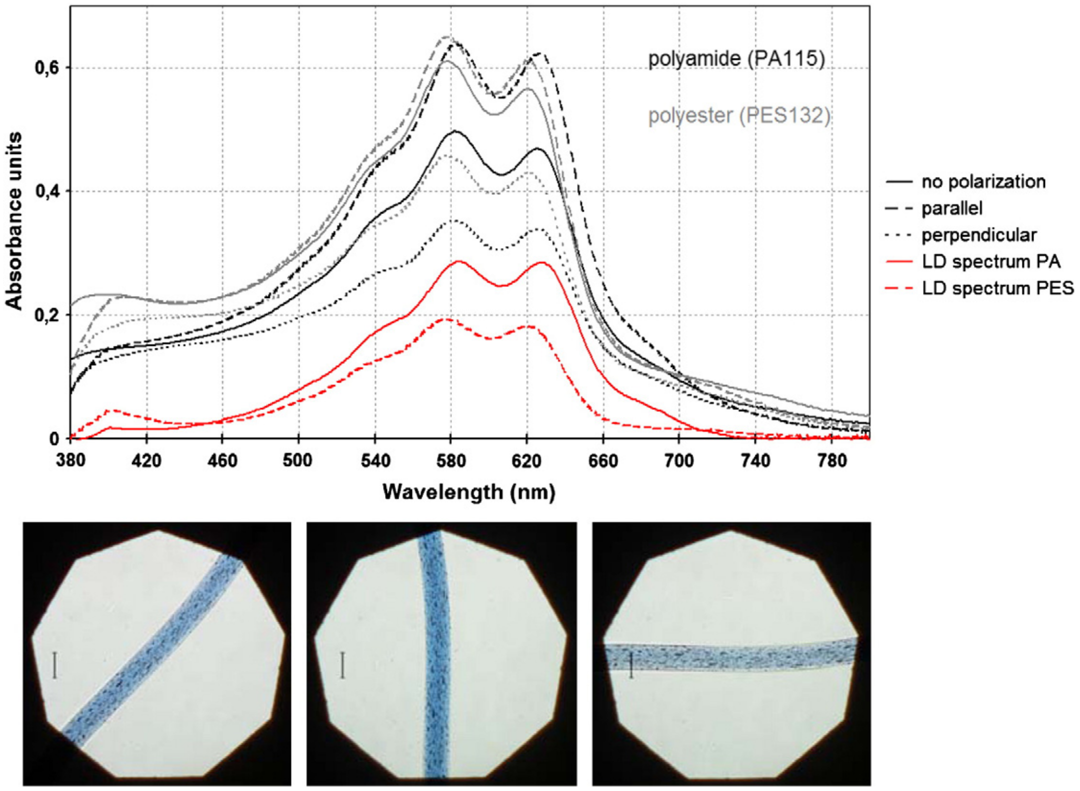

Fig. 4. Above: MSP-PPL spectra of polyamide and polyester dyed with the disperse dye Samaron Blue H3R.Below: microscopic observation of the polyamide sample in bright field (left) and with polarized light oriented respectively parallel with (middle) and perpendicular to (right) the fibre's axis.

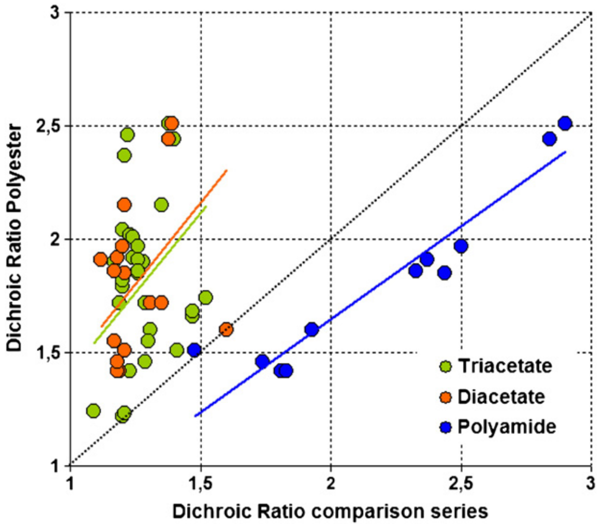

Fig. 5. Correlations of the dichroic ratio calculated for the absorption bands of disperse dyes on triacetates, diacetates and polyamides versus those found on polyesters (linear least squares, no intercept). The dotted line represents equal dichroic effects.

between the dichroic ratios observed on polyester and on acetates, in general, those of polyesters can be considered about 1.5 times higher.

A reasonable linear correlation ($r^2 = 0.89$) has been found between the dichroic ratio observed for the disperse dyes on polyamide (when allowing no intercept), $R_{(PA)}$ and on polyester, $R_{(PES)}$:

$$R_{(PES)} = 0.8236 \cdot R_{(PA)}$$

This means that, in general, the dichroic ratio of polyamides is 1.2 times higher than those found in the polyester samples. The dichroic effect for disperse dyes on the different fibre classes follows the order: PA>PES>TrAc, Ac.

4. Discussion

The dye systems encountered in this work are basic and disperse dyes. The basic dye class is characterized by its cationic character allowing Coulombic attraction if negative dye sites are incorporated in the acrylic polymer structure. Other interactions such as Van der Waals contribute to the high wet fastness properties of basic dyes on acrylics. Two distinct categories of basic dye structures exist: those which have a delocalized positive charge (azine, oxazine, triarylmethanes and xanthenes) and those possessing a localized positive charge (azo, anthraquinone and methine). Because of their improved light fastness properties, the latter is preferred nowadays. The majority of all basic dyes belong to the azo (43%), methine (17%) or triarylmethane (11%) chemical dye classes [7,8].

The compounds belonging to the disperse dye class are rather small structures without any ionic character. The interactions between these dyes and hydrophobic fibres (cellulose acetates, polyester) are hydrogen bonding, dipole–dipole and Van der Waals dispersion forces. Azo and anthraquinone structures account for about 90% of all known disperse dyes. This application class can be used for dyeing acrylics, acetates, polyamides and polyesters [7,9].

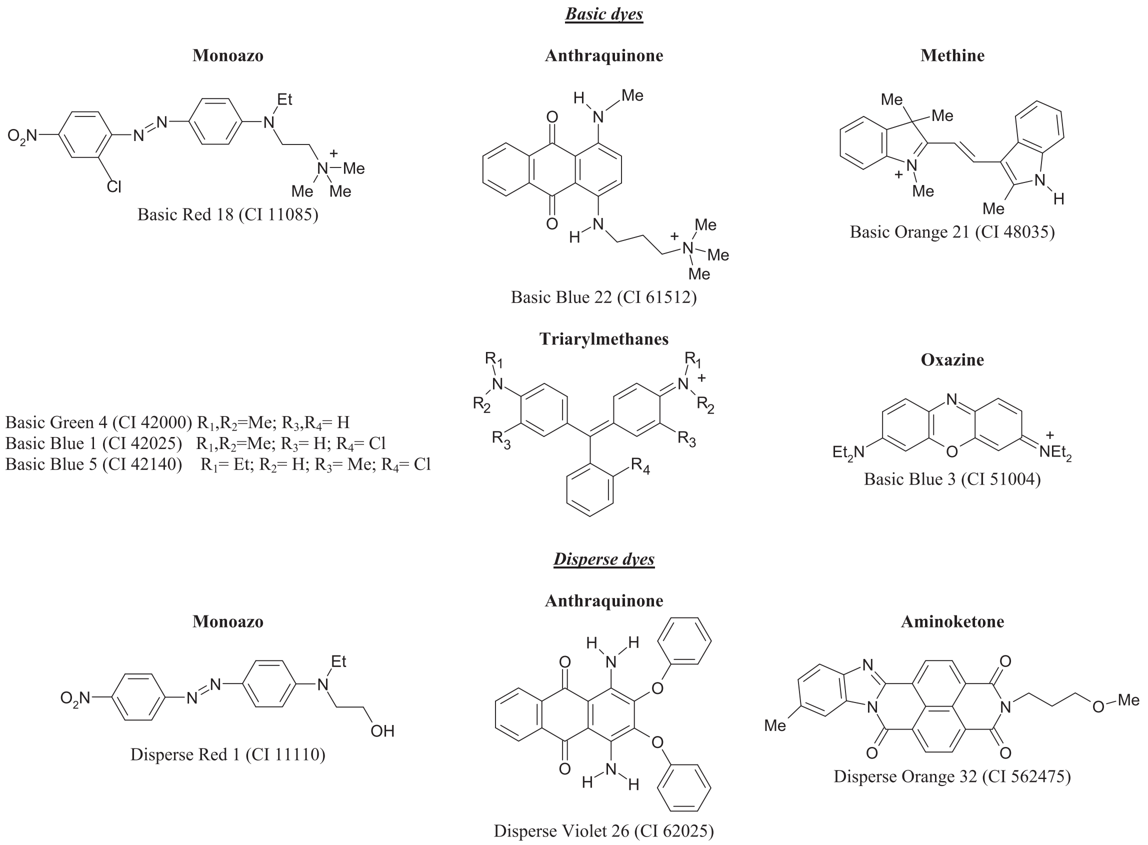

Fig. 6. Some examples of basic dye structures for acrylic fibres and disperse dye structures for acrylics, cellulose acetates, polyester and polyamide fibres.

The major chemical classes contributing to the dyeing of acrylics and cellulose acetate are represented in Fig. 6.

It is interesting to note that the dichroic effects in dyed polyamides were thought to be smaller than those encountered for dyed polyesters. Indeed, smaller dichroic effects were noted for the acid dyes on polyamide [2] than those described for the disperse dyes on polyester [1]. However, comparison of the same disperse dyes on polyamide and polyester, clearly shows that in most cases the dichroic effect is more pronounced for polyamide.

In our fibre laboratory, dichroism is checked as a routine microscopy procedure for many years. Although acrylic is one of the major fibre classes encountered in case work, on only one occasion a very weak dichroic effect was observed for a greenish grey acrylic fibre type. This means that any observable effect for acrylics should be considered as a very rare characteristic. Microscopic images and the spectral data obtained from this sample are represented in Fig. 7. The spectrum is believed to result from a dye mixture of a red dye (absorption at about 465 nm) and a blue dye (absorptions at 590 and 620 nm). The dichroic ratio is 1.1 for the red component's absorption band and about 1.2 for the blue component's absorptions. This differential intensity decrease results in a more neutral grey color in the perpendicular position, compared to the greenish grey hue in the parallel position (and also with non-polarized light). Another way of interpreting this effect is to look at the shape of the LD-spectrum which corresponds to the absorption spectrum of a faintly colored bluish sample. This means that when going from the parallel to perpendicular position a small amount of blue color content is subtracted, resulting in a more neutral grey fibre color. In Fig. 7, the color calculated from the absorption spectra and LD spectra (RGB values) was added, to illustrate the effect.

In most of the acrylic and acetate samples, the differential absorption of polarized light is small. However, measurement of the separate polarization spectra is valid whenever the absorption difference is higher than 0.01. For smaller effects, due to polarization artifacts and a lower signal-noise ratio, one should make use of polarization modulation methods instead as suggested by Drake [10]. In most of our samples the LD spectrum is above this threshold. It has also been demonstrated that the measurements are reproducible and are suited for comparison between fibre reference samples and fibre traces.

The bright basic dyes often result in deeply colored acrylic samples. Saturation effects may arise in the spectra of the parallel position with absorptions higher than 1.2 AU. Whenever possible this effect should be avoided by choosing a more convenient measurement position. For acrylics with a dogbone section, this could be realized when measuring in the less colored center.

Previous work on acid dyed polyamide, wool and silk [2] and work on cotton and viscose dyed with some direct dyes [3] showed a varying dichroic behavior of the same dye applied to other fibre substrates. No correlations have been found between the strength of the effects observed in fibre classes of similar nature. In this work, however, a correlation has been found between the dichroism observed for disperse dyes on polyamide and on polyester. The stronger effects observed on polyamide might be due to the proton donor and proton acceptor groups present in these fibre types for the formation of hydrogen bonds with the dye molecules. In polyester

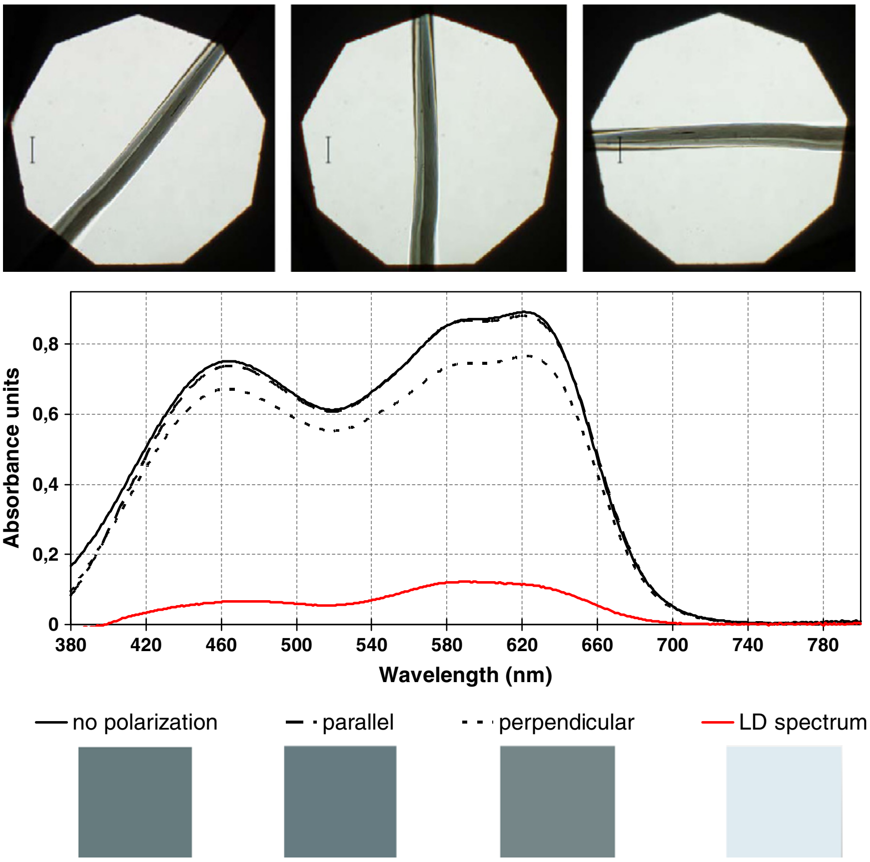

Fig. 7. Above: microscopic observation of a grey-green bean shaped acrylic fibre type from case work in bright field (left) and with polarized light oriented respectively parallel with (middle) and perpendicular to (right) the fibre's axis. Below: the corresponding absorption spectra in the parallel and the perpendicular position and the resulting LD spectrum. The squares correspond to the RGB values calculated from each of the absorption spectra and the LD spectrum.

fibres, only proton acceptor groups are present, whereas polyamides have both proton donor and acceptor groups.

These results indicate that linear dichroism is highly specific: it does not only depend on the dye structure itself but also on the surrounding molecular chains in which the dyestuffs are imbedded. In general, the absorption spectra of the same dye applied to different fibre classes recorded with non-polarized light can already give rise to spectral differences in band width, shape and position. These differences are more pronounced in the spectra with polarized light.

In this work two samples were examined which are dyed with Disperse Violet 26. These samples originate from different dye manufacturers. Surprisingly, the dichroic effect was stronger for Resolin Red Violet FBL (Bayer) than for Samaron Violet HFRL, on the triacetate as well as on the polyesters. This may be due to a difference in draw ratio of the fibre, which is another factor that contributes to the specificity of dichroic measurements. An increased draw ratio will lead to a higher orientation of the polymer chains. An orientation increase in the crystalline zones will also be accompanied by an increased orientation in the amorphous zones. It is in these amorphous zones that the dye molecules penetrate and interact with the polymer chains. As birefringence is a measure for the global fibre orientation, it comes as no surprise to find the observed weak effects in low birefringent fibres.

5. Conclusion

The basic and disperse dyes applied to acrylic fibres show a very weak positive dichroism that is very hard to observe using microscopy. The disperse dyes applied to acetates also lead to a weak positive dichroism which sometimes may be detected using microscopy. It is important to keep in mind that if the effects are weak or even if no dichroism is observed with microscopy, these can be measured using MSP-PPL.

The same disperse dyes on polyamide and polyester lead to more pronounced effects. The highest dichroic effects are observed for polyamide.

Acknowledgement

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