Talanta 123 (2014) 54–62

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Morphological, spectral and chromatography analysis and forensic comparison of PET fibers

Shady Farah [a], Tsadok Tsach [b], Alfonso Bentolila [b], Abraham J. Domb [a,b,*]

[a] Institute of Drug Research, School of Pharmacy-Faculty of Medicine, Center for Nanoscience and Nanotechnology and The Alex Grass Center for Drug Design and Synthesis, The Hebrew University of Jerusalem, 91120, Israel
[b] Division of Identification and Forensic Sciences (DIFS), Israel Police, Jerusalem, Israel

ARTICLE INFO

Article history:
Received 30 October 2013
Received in revised form
10 January 2014
Accepted 13 January 2014
Available online 5 February 2014

Keywords:
Fiber forensic comparison
Poly(ethylene terephthalate)
GPC analysis
Fiber analysis

ABSTRACT

Poly(ethylene terephthalate) (PET) fiber analysis and comparison by spectral and polymer molecular weight determination was investigated. Plain fibers of PET, a common textile fiber and plastic material was chosen for this study. The fibers were analyzed for morphological (SEM and AFM), spectral (IR and NMR), thermal (DSC) and molecular weight (MS and GPC) differences. Molecular analysis of PET fibers by Gel Permeation Chromatography (GPC) allowed the comparison of fibers that could not be otherwise distinguished with high confidence. Plain PET fibers were dissolved in hexafluoroisopropanol (HFIP) and analyzed by GPC using hexafluoroisopropanol:chloroform 2:98 v/v as eluent. 14 PET fiber samples, collected from various commercial producers, were analyzed for polymer molecular weight by GPC. Distinct differences in the molecular weight of the different fiber samples were found which may have potential use in forensic fiber comparison. PET fibers with average molecular weights between about 20,000 and 70,000 g mol^{-1} were determined using fiber concentrations in HFIP as low as 1 μg mL^{-1}. This GPC analytical method can be applied for exclusively distinguish between PET fibers using 1 μg of fiber. This method can be extended to forensic comparison of other synthetic fibers such as polyamides and acrylics.

1. Introduction

Fibers are an important class of forensic and trace evidence that can provide valuable information to support an association between individual or individuals and a crime scene. Standard forensic examinations for man-made fibers consist of microscopic techniques such as visible light, polarized light, and fluorescence microscopy, followed by microspectrophotometry. If, after that stage, two fibers are still indistinguishable, they are then examined by infrared spectroscopy, which is used to identify the fiber polymer type present. This is sometimes followed by dye extraction and analysis.

Man-made fibers such as polyesters, polyamides and polyacrylics have been analyzed for industrial purposes by various methods, including FTIR and Raman spectroscopy, circular dicroism, wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and transmission electron microscopy (TEM) [1].

Due to the wide scope of samples typically found in a forensic investigation and the minute size of those samples, a variety of spectroscopic techniques may be needed. IR spectroscopy has been effective to identify fibers such as acrylics, polyamides, or polyesters. The size of the sample may require the use of microscopic IR spectroscopy, and the nature of the sample may require the use of external reflection spectroscopy or attenuated total reflectance spectroscopy [2,3]. The dichroic behavior of pigmented fibers depends strongly on the crystal structure (shape of the pigment grains) and the draw ratio (orientation of the polymer chains) as has been reported [4]. A comprehensive review of research and advances in scientific methodologies relating to the forensic examination of fibers has been reported with little attention to fiber polymer molecular weight [5]. The use of chromatography and time-of-flight mass spectrometry for the determination of disperse dyes extracted from fibers has also been reviewed [6].

Forensic comparison of fibers has traditionally focused on morphological analysis as well as on spectral analysis. As fibers and textiles are mass produced a fiber cannot be positively identified as having come from a particular textile source. But multiple transfers, numerous fibers, batch variation, environmental effects, rarity of the fiber and other factors may increase the significance of the association.

* Corresponding author at: Institute of Drug Research, School of Pharmacy-Faculty of Medicine, Center for Nanoscience and Nanotechnology and The Alex Grass Center for Drug Design and Synthesis, The Hebrew University of Jerusalem 91120, Israel. Tel.: +972 26757573; fax: +972 26757076.
E-mail address: avid@ekmd.huji.ac.il (A.J. Domb).

http://dx.doi.org/10.1016/j.talanta.2014.01.041
0039-9140

GPC is known as a rapid and reliable method for determining the molecular weight distribution of polymers. The limited solubility of PET in common organic solvents presents difficulties in its characterization in solution, especially in the determination of molecular weight and molecular weight distribution. Early trials, using m-cresol at high temperature as a GPC-solvent were rather unsuccessful due to degradation of the polymer. Subsequently, mixtures of m-cresol/chloroform, o-chlorophenol/chloroform, or 1,1,2,2-tetrachlorothane/nitrobenzene allowed measurement at room temperature, but these procedures still needed extended heating to dissolve the samples [7,8]. Drott reported the use of HFIP as a GPC solvent for PET as well as for nylon-6,6 [9]. Disadvantages of this method, however, are the insolubility of polystyrene standards in pure HFIP, the partial incompatibility of GPC columns filled with crosslinked polystyrene, and the high cost of HFIP Samples [10]. Chloroform containing 2 vol% HFIP can be used as a new solvent for routine GPC analysis of PET [8].

The use of GPC in examinations for the forensic identification of polymer products (fibers, tail light lens fragments, plastic parts etc.) for molecular weight determination was suggested as early as 1979, however very little has been reported about the use of GPC in fiber comparison [11]. An automated system was described for the routine forensic identification of polymers (e.g., styrene-acrylonitrile copolymer, polyethylene glycol terephthalate, or cellulose nitrate) by the determination of oligomers and other low-molecular weight components using size exclusion chromatography (SEC) and reversed-phase chromatography [12]. The state of the art and the most recent advances in the forensic characterization of polymeric items was recently reviewed, but little attention has been given to molecular fiber analysis or GPC [13]. It is our objective to investicate available methods for the comparison analysis of PET fibers using microgram amounts of fibers. Of particular interest, is the implementation of a simple, easy to apply and robust high certainty method in the routine analysis for the comparison of man-made fibers. The hypothesis is that molecular analysis of fiber samples can provide a distinctive comparison among fibers. Thus, methods for molecular weight analysis, i.e. GPC, are applied to obtain a desired comparison methodology for fibers analysis.

2. Experimental

2.1. Materials

14 plain PET fiber samples supplied by German manufactures and wholesalers were divided by microscopic examination into pairs in two groups, A and B as follow [14]: A1 Trevira T-298, 1,7 dtex/38 mm, semi-dull, PTA route and B1 Trevira FM 04/09,DMT route, (Trevira GmbH, D-86397 Bobingen, Germany); A2 Terital Typ 15, 1,5 dtex/38 mm, dull and B2 Dacron Sabanaci, 1,5 dtex/38 mm, dull (Leinefelder Textilwerke GmbH, D-37327 Leinefelde, Germany); A3 Diolen 57 T, dull, filament yarn (Diolen, D-63784 Obernburg, Germany); B3 PET Type 710, dull, filament yarn, (Performance Fibres GmbH, D-86399 Bobingen, Germany); A4 Trevira 350, Partie 1355, 1,7 dtex/38 mm (Trevira GmbH, D-86397 Bobingen, Germany); B4 Hydropur Typ IADA 037, 1,7 dtex/38 mm (Leinefelder Textilwerke GmbH, D-37327 Leinefelde, Germany); A5 Trevira 270, batch 1721, 1,7 dtex/38 mm, bright Trevira, (Trevira GmbH, D-86397 Bobingen, Germany); B5 Dacron 158 NSD (Advansa GmbH, D-59071 Hamm-Uentrop); A6 Grisuten 22, 3,3 dtex/60 mm, semi-dull and B6 Grisuten 24, 3,3 dtex/60 mm, semi-dull (Märkische Faser GmbH, D-14727 Premnitz, Germany); A7 Polyester (PET), dyed with 1% *Dianix* and B7 Polyester (PET), dyed with 1% *Resolin* (Dystar, D-65923 Frankfurt/Main, Germany), 1,1,1,3,3,3-Hexaflouroisopropanol 99.8% Ar, anhydrous basis (HFIP, Bio Lab), Chloroform, Ehanol and Acetonitrile (J.T.Baker), Chloroform-D, Toluene, Dimethyl sulfoxide, Dimethylforamide, Tetrahydrofuran, Trifluoroacetic acid, Nitrobenzen, p-Xylene, Cersol, Phenol, α Cyano 4-Hydroxycinnamic acid, 2,4,6-Trihydroxyacetophenone and Diammonium Hydrogen Citrate, all were purchased from Sigma Aldrich (Rehovot, Israel).

2.2. Methods

2.2.1. Brightfield, polarized light, and fluorescence microscopy [14]

Samples were mounted on glass slides using Phytohistol®. Microscopy of fiber samples was performed using Leica DMRP microscopes equipped with a Leica FS-CB comparison bridge. The fluorescence data of the fibers for excitation with UV, blue and green light were recorded with Leica excitation/filter combinations A, E4 and M2. The range of diameters of the fiber samples was measured with a Leitz ocular micrometer.

2.2.2. Melting range determination (hot stage microscopy) [14]

The melting range of the fiber samples was determined by hot stage microscopy on glass slides (dry mounting) using a Mettler-Toledo FP 90 System with a Mettler-Toledo FP 82 hot stage equipped to a Leitz Ortholux microscope. The data given are the range of melting points resulting from three runs for each sample at a heating rate of 2 °C/min.

2.2.3. Interference microscopy [14]

The refractive index of a fiber, Δn, is: $n_{para} - n_{ortho}$, where n_{ortho} is defined as the refractive index of a fiber orthogonal to the fiber axis, n_{para} is defined as the one parallel to the fiber axis; n_{para} and n_{ortho} were determined utilizing a Jenapol Interphako Interference microscope and equirefractive immersions of the fibers on glass slides according to the Method reported by Heuse, O. and Adolf, F.P. [15]. Immersion media with refractive indices ranging from 1.400 to 1.800 (sets AA, A, B and M, stepwidth 0.002 and 0.005, respectively) were obtained from Cargille Labs, USA.

2.2.4. Atomic force microscopy (AFM)

Fibers were suspended in ethanol and then fixed on glass slides, followed by fast drying. Surface topography of the fixed fibers were scanned with Dimension 3100 scanning probe microscope with a Nanoscope-V controller (Bruker, Germany) by using Tapping Mode (TM), topography was obtained by lightly tapping the surface with the oscillating Si probe (RTESP probe, Bruker, Germany) at $f=300$ kHz. Two points on each fiber sample were analyzed, and the analysis was performed in triplicate with the following parameters: Spectral period 1.64 μm, spectral frequency 0.608 μm, and spectral RMS amplitude 22.0 nm (Analysis Key: Bright close to the top, dark deeply to the bottom) were used.

2.2.5. Differential scanning calorimetry (DSC)

Fiber samples (4–5 mg) were weighted by micro analytical balance ±1 μg and the thermal properties were measured using Metler TA 4000-DSC differential scanning calorimeter, at a heating rate of 10 °C/min (0–180 °C) and on a Stuart Scientific Melting point SMP1 heater. Weight loss was traced and detected by micro analytical balance.

2.2.6. Smart internal reflection (iTR)

The samples were analyzed by Smart iTR instrument, Nicolet iS10 (Thermo Scientific company, USA), PET fiber samples were placed directly on the diamond Nicolet, and then were scanned in interval 500–4000 cm^{-1}. The spectra were evaluated with OMNIC software for spectrums similarity% calculations. Fibers were analyzed using two methods: (i) native fiber surface scanning and (ii) fiber film scanning. Fiber films were prepared by dissolving 5 mg samples

Table 1
Fiber characterization using microscopy analysis based on Brightfield, polarized light, and fluorescence microscopy, interference microscopy and melting point determination using hot stage microscopy [14].

Fiber analysis	A1	B1	A2	B2	A3	B3	A4
Color	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
Cross section	Round	Round	Round	Round	Round	Round	Round
Delustrant	++	++	+	+	+	+	++
UV-Fluorescence	Blue	Blue	Blue	Blue	Blue	Blue	Blue
BL-Fluorescence	Green	Green	Green	Green	Green	Green	Green
GN-Fluorescence	None	Red	None	None	Red[b]	None	None
Diameter (μm)	11.5–14.0	11.5–14.0	12.0–13.5	12.0–13.5	21.5–23.5	21.5–23.5	11.5–13.0
n_{para}	1.700	1.698	1.715	1.715	1.715	1.720	1.696
n_{ortho}	1.544	1.548	1.544	1.544	1.538	1.546	1.546
Δn	0.156	0.15	0.171	0.171	0.177	0.174	0.15
Melting point(°C)	257–259	255–258	259–268	259–261	258–262	256–258	261–262
	B4	**A5**	**B5**	**A6**	**B6**	**A7**	**B7**
Color	Colorless	Colorless	Colorless	Colorless	Colorless	Blue–green	Blue–green
Cross section	Round	Round	Round	Round	Round	Round	Round
Delustrant	++	+	+	++	++	+	+
UV-Fluorescence	Blue	Blue	Blue	Blue	Blue	Blue	Blue
BL-Fluorescence	Green	Green	Green	Green	Green	Green	Green
GN-Fluorescence	Red[b]	Red	Red	None	None	Red	Red
Diameter (μm)	11.5–13.0	12.0–13.5	12.0–13.5	17.5–18.5	16.0–16.5	15.5–23.5	15.5–23.5
n_{para}	1.692	1.705	1.700	1.710	1.710	N.F.[a]	N.F.[a]
n_{ortho}	1.546	1.542	1.544	1.546	1.542	N.F.[a]	N.F.[a]
Δn	0.146	0.163	0.156	0.164	0.168	–	–
Melting point(°C)	256–261	251–254	257–259	254–256	254–255	262–264	262–264

[a] Highly textured. Interference microscopy not feasible.
[b] Very weak.

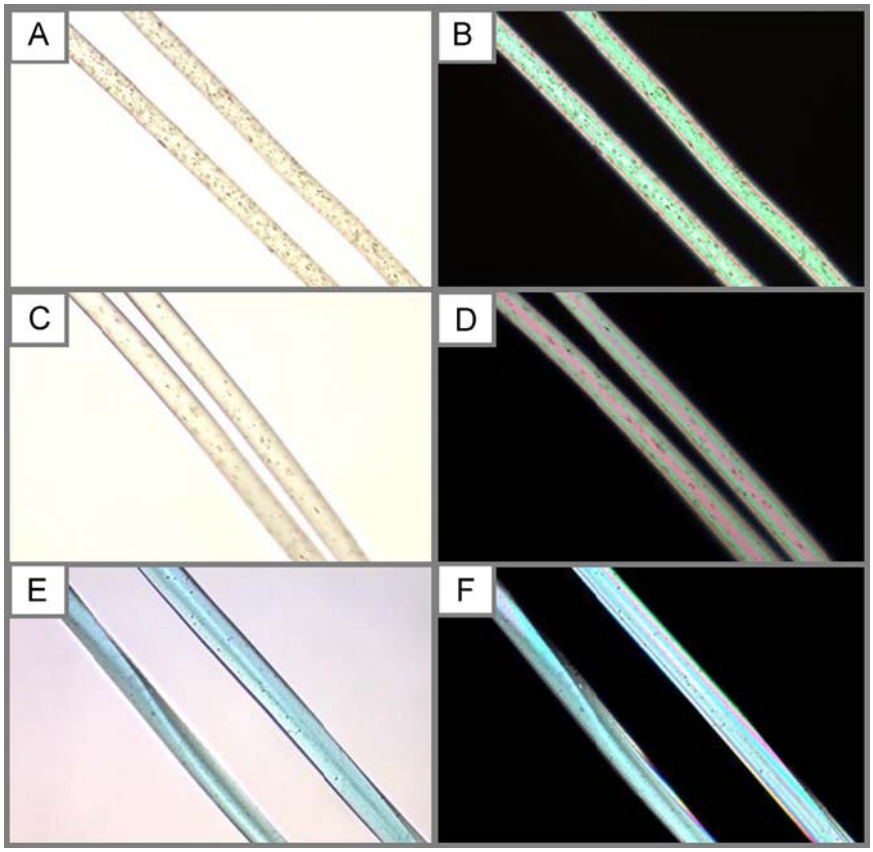

Fig. 1. Microscopy of polyethylene terephthalate (PET) fibers: (A) Brightfield and (B) Polarized light microscopy of fiber pairs; A1 (Right) and B1 (Left), Trevira GmbH, D-86397 Bobingen, Germany. X40 Magnification; (C) Brightfield and (D) Polarized light microscopy of PET fiber pairs; A2 (Right) and B2 (Left), Leinefelder Textilwerke GmbH, D-37327 Leinefelde, Germany. X40 Magnification; (E) Brightfield and (F) Polarized light microscopy of PET fiber pairs: A7 (Right) and B7 (Left), Dystar, D-65923 Frankfurt/Main, Germany. X40 Magnification [14].

in 100 μL of HFIP followed by fast evaporation over a Teflon coated plate.

2.2.7. Solubility test

1 mg fiber sample was accurately weighted and tested for its solubility in the following solvents: toluene, dimethyl sulfoxide (DMSO), dimethylforamide (DMF), tetrahydrofuran (THF), chloroform, nitrobenzen, p-xylene, cresol, phenol and hexafluoro isopropanol (HFIP).

2.2.8. H^1-nuclear magnetic resonance (H^1-NMR)

5 mg fiber sample was weighted accurately and dissolved in 200 μL HFIP and 1 mL of chloroform-D was added and mixed until a clear homogenous solution was obtained. H^1-NMR spectra were recorded using Varian 300-MHz spectrometer in 5 mm o.d. tubes. Values were recorded as ppm relative to the internal standard tetramethylsilane (TMS).

2.2.9. High resolution-scanning electron microscopy (HR-SEM)

Samples were placed on a conductive carbon paper and coated with Au/Pd gold to a thickness of about 10 nm using a sputtering deposition machine (Polarone E5100). Coated fibers were imaged using high resolution SEM, Sirion, (FEI Company, Netherlands) at an acceleration voltage of 30 kV with a Shottky type field emission source and a secondary scattered electron detector (SE). Fibers were analyzed for their shape and dimension.

2.2.10. Flow injection mass spectrometry

PET fibers with a concentration of 0.1 mg mL^{-1} in HFIP were prepared and then scanned at intervals of 0–2000 m/z using HPLC-MS/MS system (Thermo Scientific, San Jose, CA, USA) included an Accela Pump with degasser module and an Accela Autosampler connected to a TSQ Quantum Access Max mass spectrometer via a heated electrospray ionization (H-ESI) interface. TSQ Tune Software (Thermo Scientific, San Jose, CA, USA) was used for the acquisition. Data processing was carried out using the Xcalibur program (Thermo Scientific, San Jose, CA, USA). All 7 fiber pairs were analyzed, and their MS spectra were compared. Part of the fibers were identified with 3 densities: low density (LD), medium density (MD), and high density (HD). All of these densities were also analyzed and compared by spectrum overlaying. Samples were run in duplicate.

2.2.11. MALDI-TOF MS

0.1 mg PET fiber samples were weighted and dissolved in 100 μL HFIP, then the samples were affixed onto different matrices followed by solvent evaporation. 3 matrices were chosen and prepared as follows: (A) 10 mg mL^{-1} α cyano 4-hydroxycinnamic acid in 1:1 0.1% trifluoroacetic acid:acetonitrile, (B) 10 mg mL^{-1} α cyano 4-hydroxycinnamic acid in 4:1:6 water:3% trifluoroacetic acid:acetonitrile, and (C) 2,4,6-trihydroxyacetophenone in 50 mg mL^{-1} diammonium hydrogen citrate in 50% acetonitrile. Fiber analysis were conducted by Voyager DE-PRO mass spectrometry (Applied iosystems-ABI, USA). A gridless ion source was equipped with a nitrogen laser (337 nm) and a reflector. All spectra were acquired in the reflector's

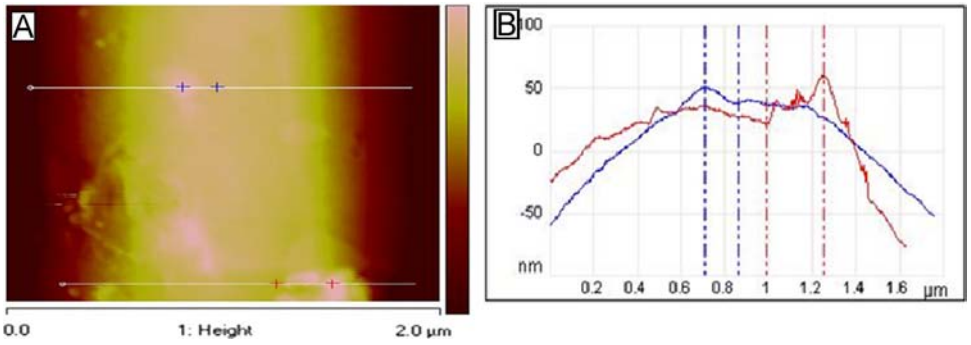

Fig. 2. (A) Individual B1 fibers at two different areas were scanned. (B) Surface topography profiles of the two analyzed areas (blue and red), conducted by Dimension 3100 scanning probe microscope with a Nanoscope-V controller (Bruker, Germany) by using Tapping Mode (TM), topography was obtained by lightly tapping the surface with the oscillating Si probe (RTESP probe, Bruker, Germany) at $f=300$ KHz, (Spectral period 1.64μm, spectral frequency 0.608 μm^{-1} and spectral RMS amplitude 22.0 nm). The results show that the fiber surface is not uniform.

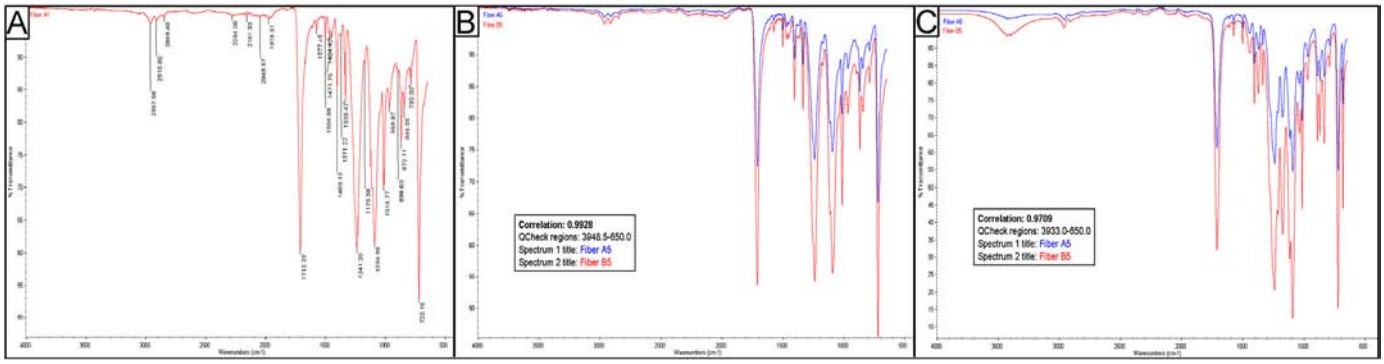

Fig. 3. PET fibers iTR spectra, PET samples analyzed by Smart iTR instrument, Nicolet iS10, PET fiber samples placed directly on the diamond Nicolet and scanned in intervals of 500–4000 cm^{-1}. Spectrum (A) Fiber A1 analyzed by native fiber direct surface scanning, 2967 cm^{-1} (=C–H, aromatic), 2915 cm^{-1} and 2849 cm^{-1} (C–H, aliphatic), 1713 cm^{-1} (C=O, ester bond), 1504 cm^{-1} (C=C), 846 cm^{-1} and 872 cm^{-1} para disubstituted aromatic ring. Spectrum (B) Fibers pair A5 and B5 overlapping, analyzed by native fiber direct surface scanning, overlapping% was found to be 99.3% and (C) Fiber pair A5 and B5 overlapping, analyzed by fibers films scanning, overlapping%—97.0% was found.

positive ion mode with an acceleration voltage of 25 kV and a reflector voltage of 26.3 kV. The detector m/z range was 20.0–80.0 kDa to exclude high intensity signals arising from low mass ions and to cover the entire PET mass spectrum. The laser intensity was set to the maximum value possible to acquire high resolution spectra, which were gathered by irradiating 40–50 different positions at the center area on the sample spot, with a total of 2500 shots per sample. Time-to-mass conversion of time-of-flight mass spectra was achieved using a self-calibration method [7,16]. All spectra were treated using Voyager software (USA).

2.2.12. Gel permeation chromatography (GPC)

PET Samples and polystyrene standards (standards with average molecular weights (Mw) of: 5.6–524.0 kDa) were analytically weighted in 5 mL vail, dissolved in 1 mL 4% v/v HFIP in chloroform and then solutions were filtered over cotton directly into GPC vials. Samples analysis conducted in parallel with both detectors UV (254 nm, Waters 484 Absorbance Detector-UV (USA)) and Refractive Index (RI Detector 410, 40 °C, USA) using GPC System Waters 717 plus Autosampler (USA) and Waters 1515 Isocratic HPLC Pump (USA). The system was equipped with Styragel HR4 Column, 5 μm, 7.8 × 300 mm (WAT044225, Mw 5.0–600.0 kDa, Ireland), mobile phase 2% v/v HFIP in chloroform, flow 1 mL min^{-1}, 30 μL injected volume and 20 min run time per sample. Each fiber was analyzed in triplicate, and twice injected. The sensitivity limit of the GPC analysis method for fibers molecular characterization conducted at the following concentration: 1, 2, 4, 10, 100 and 1000 μg per 1 mL 4% v/v HFIP in chloroform, diluted solutions were prepared by using Hamilton Microliter™ Syringes. GPC data was given as Weight-average molecular weight (Mw), Number-average molecular weight (Mn) and Peak molecular weight (Mp—molecular weight at the highest point of the peak).

3. Results and discussion

Fibers were characterized by visualization microscopy as brightfield, polarized light, fluorescence, and interference microscopy followed by melting range determination using hot stage microscopy. Fibers were similar and difficult to differentiate by Microscopic analysis as summarized in Table 1 and Fig. 1 [14]. Topography and surface morphology of these fibers was determined by AFM surface scanning. The surface topology is not consistent and changes along the fiber as demonstrated in representative Fig. 2, thus this analytical method was not further investigated. Thermal analysis of PET fiber pairs was determined by DSC for glass transition temperature (T_g), melting point (T_m),

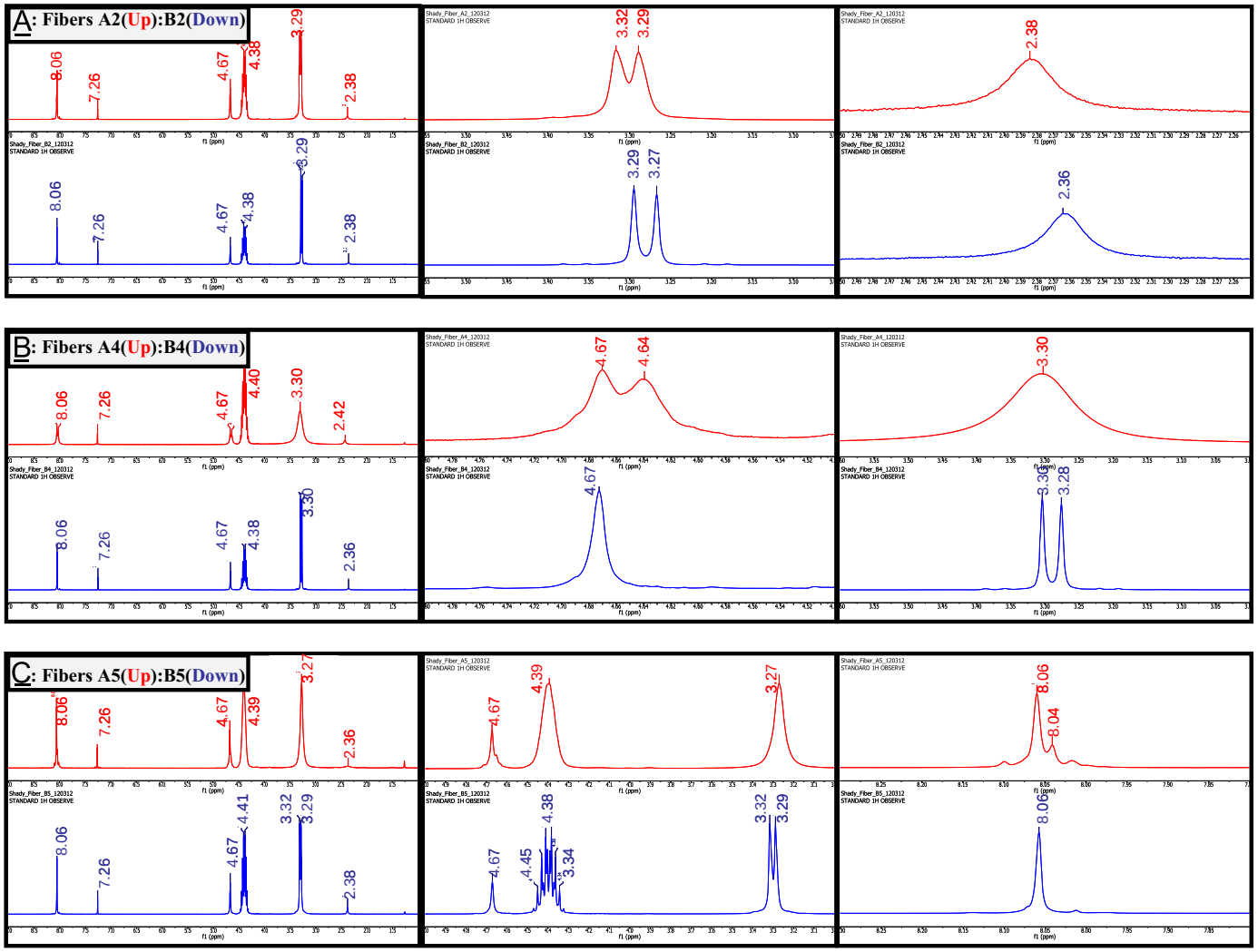

Fig. 4. A–C showing differences in H^1 NMR spectra of PET fiber pair overlays, A2:B2 (Spectrums interval: 1–9 ppm, 3–3.50 ppm and 2.25-2.50 ppm), A4:B4 (Spectrums interval: 1–9 ppm, 4.50–4.80 ppm and 3–3.60 ppm) and A5:B5 (Spectrums interval: 1–9 ppm, 3–5 ppm and 7.80–8.30 ppm) respectively. Peak shifting and different splitting were found in pair spectra comparison. H^1 NMR ($CDCl_3$: HFIP mixture, ppm), 2.36 (s, 1H, HFIP), 4.43 (m, 1H, HFIP), 3.12 (d, solvent mixture), 4.50-4.70 (t, 4H, O═C–O–CH_2–CH_2–O–C═ONH2), 8.00-8.25 (d, 4H, aromatic benzene ring's protons).

and decomposition temperature. A comparison of fiber thermal profiles showed minor difference among the fiber pairs in T_g, T_m, and decomposition temperatures. Differences in weight loss upon heating were found to be negligible.

Functional groups of the PET fibers were analyzed using *Smart iTR* spectroscopy. The fibers were analyzed with two methods: (i) native fiber surface scanning, and (ii) fiber film scanning. Fig. 3 shows the iTR spectra for PET fibers. Spectra overlap similarity in the first method was found to be: 94.5–99.6%; while in the second method: 84.5–94.0% (Fibers: Ax:By$\leftrightarrow$x=y). However, cross analysis overlapping (Fibers: Ax:By$\leftrightarrow$x$\neq$y), for method (i) was found to be: 92.0–99.0%; while in method (ii): 61.1–77.9%. These results indicate that PET fibers difference are more frequently located at the fiber core, which corresponds to minor chemical modification on the polyester chains or to different side groups attached to PET fiber chains.

For PET fibers H^1 NMR, MS, Maldi-TOF-MS, and GPC analysis, an affordable solvent for PET is required. Accordingly, a solubility test for PET fibers was conducted in organic solvents, and they were found to be highly soluble at room temperature in hexafluoro isopropanol (HFIP), while solubility in phenol/cresol/dimethylforamide was found to be partial with heating. No solubility at all was found in solvents, including toluene, dimethyl sulfoxide, acetonitrile, short aliphatic alcohols, tetrahydrofuran, chloroform, nitrobenzene, and p-xylene with/without heating. H^1 NMR analysis showed differences in spectra analysis; the differences includeed: peak shifts, different peak splitting, and the appearance of new peaks as shown in Fig. 4. HR-SEM analysis was conducted for the 7 fiber pairs. The results give a comprehensive

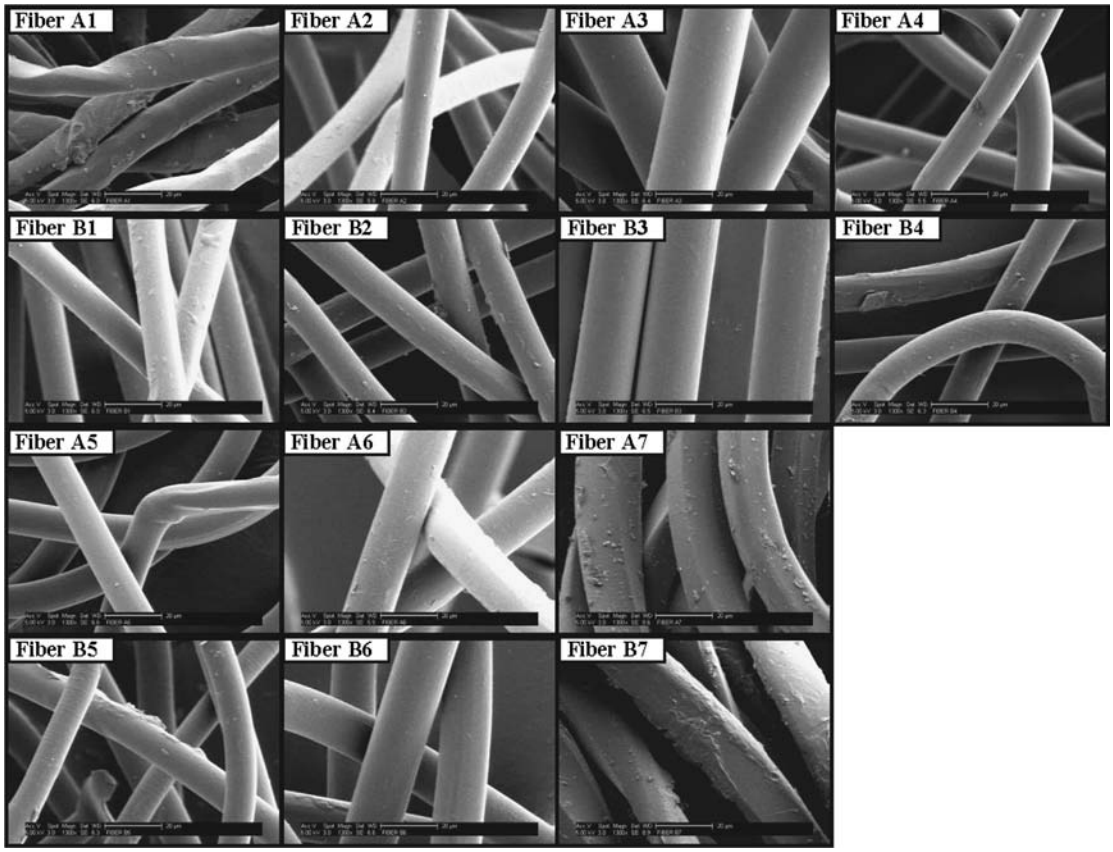

Fig. 5. HR-SEM analysis of 14 PET fibers (7 pairs), conducted using Sirion, (FEI Company, Netherlands) at an acceleration voltage of 30 kV and secondary scattered electron detector (SE). Magnification 1300 X.

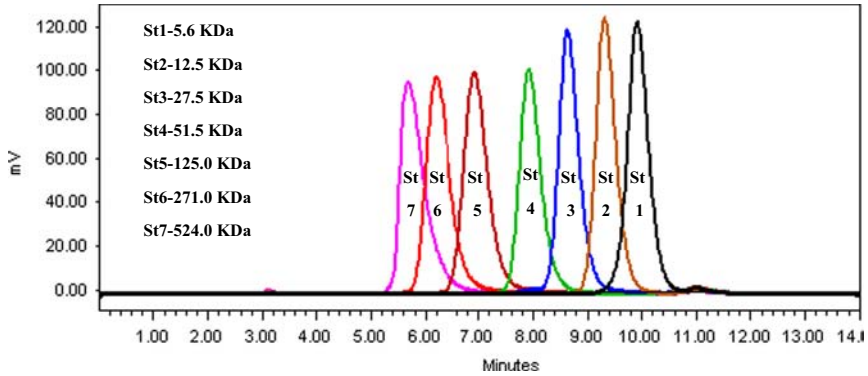

Fig. 6. Polystyrene standards eluted at the following GPC conditions: 1 mL min^{-1} of 2% v/v HFIP in chloroform, UV detection at 254 nm, injection of 30 μL of 1 mg mL^{-1} polystyrene standard in 4% v/v HFIP in chloroform. St1 through St7 are the reported molecular weights of polystyrene standards. Linear line: log Mw=8.17e000–4.39e-001 T^1, R^2=0.9946.

view of the different types and shapes of fibers. The data are summarized in Fig. 5.

14 fibers were analyzed by MS for low molecular weight differences 0–2.0 kDa. Part of the fibers were identified with 3 densities: low density (LD), medium density (MD), and high density (HD). All of the samples were analyzed in duplicate. MS data showed that the majority of the peaks were identical, and differences were found above 1.3 kDa. Maldi-TOF-MS with a wide range scanning 20.0–80.0 kDa was applied to fiber samples fixed onto 3 different matrices. In attempts to estimate different Mw evaluations according to matrix type, no individual peaks were found except for matrix A (10 mg mL^{-1} α cyano 4-hydroxycinnamic acid in 1:1 0.1% trifluoroacetic acid:acetonitrile). Background noise was still clearly viewed.

GPC was used for the determination of fiber molecular weight. The limited solubility of PET in common organic solvents led to serious difficulties in its characterization in solution, especially in the determination of molecular weights and molecular weight distribution. Early trials using m-cresol or m-cresol/chloroform or at high temperature as a GPC-solvent were apparently unsuccessful due to degradation of the polymer. Drott reported the use of HFIP as a GPC solvent for PET as well as for nylon-6,6 [9]. Wisskopf reported the presence of chloroform containing 2 vol% HFIP as a new solvent for the routine GPC analysis of PET [8]. Consequently, a mobile phase was chosen, PET samples and polystyrene standards were analyzed in two concentrations — 0.1 mg and 1 mg mL^{-1} (4% HFIP in chloroform v/v, $n=3$) — with two detectors UV (254 nm) and refractive index (RI), and each sample was injected twice with 30 μL injection volume. RI detector was limited in detecting concentrations of mg mL^{-1} and thus was not further used in this study. Fig. 6 shows the chromatogram of the polystyrene standards, providing a correlation between the molecular weight and retention time that was used calculation of the molecular weigh of the fiber samples. Table 2 summarizes the calculated Weight-average molecular weight (Mw), Number-average molecular weight (Mn) and Peak molecular weight (Mp—molecular weight at the highest peak) for each fiber sample. Fig. 7 shows the chromatograms of all analyzed fibers.

GPC analysis succeeded in clarifying the differences between fiber pairs, which were found to be very similar by the other analytical methods described above. Fig. 8 presents a comparison between two pairs of fibers. Thus, GPC provided an accurate tool to distinguish among the tested fibers. Fig. 9 shows representative spectra of analyzed fibers with high reproducibility. All fibers differ in all three calculated molecular weights so any of Mw, Mn or Mp could be used to distinguish among fibers. It might be useful to develop a single parameter that take in account all three results, for example, 0.33Mw+0.33Mn+0.33Mp, or use Mw and Mn for calculating the single parameter.

Method limit of detection at low concentrations of fiber polymer solution was examined by analyzing solutions with concentrations as low as 1 μg mL^{-1}. It was found that concentrations of 1 μg mL^{-1} with an injection volume of 30 μL provide a measurable peak as shown in Table 3 and Fig. 10. Similar results were obtained for all tested fibers at high reproducibility.

Table 2
Mn, Mw and Mp of PET fibers analyzed by GPC (see conditions in Fig. 7).

Fiber sample	Mn[a*] (kDa**)	Mw[b*] (kDa**)	Mp[c*] (kDa**)
A1	**24.4 ± 0.1**	**44.2 ± 0.3**	**40.1 ± 1.4**
B1	**27.7 ± 0.6**	**50.6 ± 1.8**	**46.0 ± 1.6**
A2	**27.5 ± 0.1**	**49.3 ± 0.5**	**43.7 ± 1.4**
B2	**24.8 ± 0.4**	**45.8 ± 1.1**	**40.6 ± 1.0**
A3	**31.0 ± 0.6**	**61.0 ± 1.8**	**54.4 ± 2.3**
B3	**34.0 ± 0.7**	**66.5 ± 1.5**	**64.4 ± 1.8**
A4	**18.9 ± 0.5**	**28.6 ± 1.0**	**21.8 ± 1.6**
B4	**26.8 ± 0.5**	**49.2 ± 1.2**	**44.6 ± 1.2**
A5	**22.7 ± 0.5**	**40.0 ± 1.3**	**32.5 ± 1.1**
B5	**27.1 ± 0.5**	**48.9 ± 1.1**	**45.4 ± 1.1**
A6	**24.7 ± 0.6**	**45.2 ± 1.5**	**37.5 ± 2.1**
B6	**22.4 ± 0.3**	**38.4 ± 0.8**	**32.8 ± 0.8**
A7	**24.1 ± 0.5**	**44.2 ± 1.6**	**35.8 ± 1.0**
B7	**24.2 ± 0.4**	**44.7 ± 1.2**	**38.8 ± 1.1**

[a] Mn: Number-average molecular weight.
[b] Mw: Weight-average molecular weight.
[c] Mp: Molecular weight at the highest point of the peak.
* Mean ± SD, ($n=3$). Each sample was injected twice.
** kDa—Kilodaltons.

4. Conclusions

Among the methods used for the analysis of a set of plain PET fibers, GPC is a practical method for PET fiber comparison with high certainty at 1 μg sample size. This method allows reproducible and accurate analysis of microgram amount of single fibers, which can be used for determining if two given fibers are from the same source or not. This method can be used for the comparison of other synthetic fibers as well as polymers and plastics. GPC can be easily applied for forensic comparison of fibers collected from a crime scene. GPC systems are relatively affordable as any HPLC system can be converted into GPC by selecting the proper column and molecular weight calculation software. This method should be explored as reliable and reproducible tool for fiber comparison.

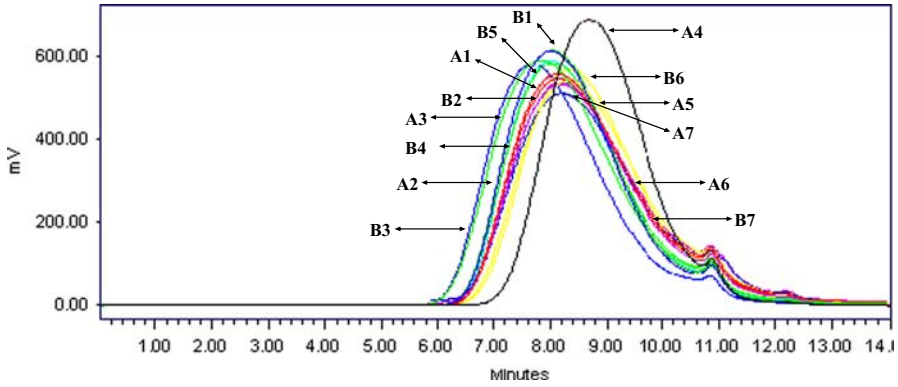

Fig. 7. PET fiber chromatograms of 14 different fiber samples collected from various commercial producers, marked by A1-7 and B1-7. The calculated molecular weights are given in Table 2. Fibers were analyzed by GPC using UV at 254 nm, mobile phase 2% v/v HFIP in chloroform at a flow rate of 1 mL min^{-1} and 30 μL injection volume of 1 mg mL^{-1} fiber solution.

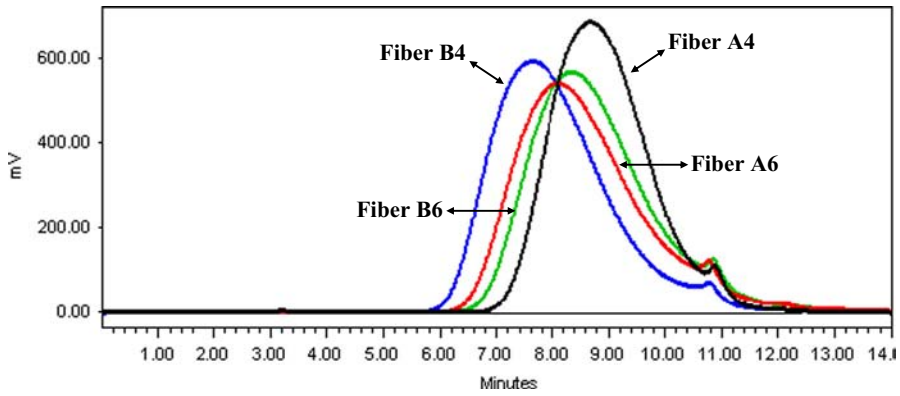

Fig. 8. PET fiber spectra of pairs of fibers, 4A, 4B, 6A and 6B. The calculated molecular weights are given in Table 2. GPC conditions are same as in Fig. 7.

Table 3
Representative fiber analysis by GPC for diluted fiber/polymer concentration (see conditions in Fig. 7).

Fiber Sample Concentration (μg mL^{-1})	Mn[a*] (kDa[**])	Mw[b*] (kDa[**])	Mp[c*] (kDa[**])
1000	27.4 ± 0.4	45.4 ± 0.1	41.2 ± 0.3
100	27.6 ± 0.4	45.3 ± 0.1	41.0 ± 0.2
10	27.9 ± 0.2	45.9 ± 0.1	41.5 ± 0.3
4	27.7 ± 0.1	45.3 ± 0.4	40.7 ± 0.4
2	27.7 ± 0.1	44.9 ± 0.4	41.9 ± 1.5
1	27.7 ± 1.4	44.9 ± 1.8	41.0 ± 0.9

[a] Mn: Number-average molecular weight.
[b] Mw: Weight-average molecular weight.
[c] Mp: Molecular weight at the highest point of the peak.
* Mean ± SD, (n=3). Each sample was injected twice.
** kDa—Kilodaltons.

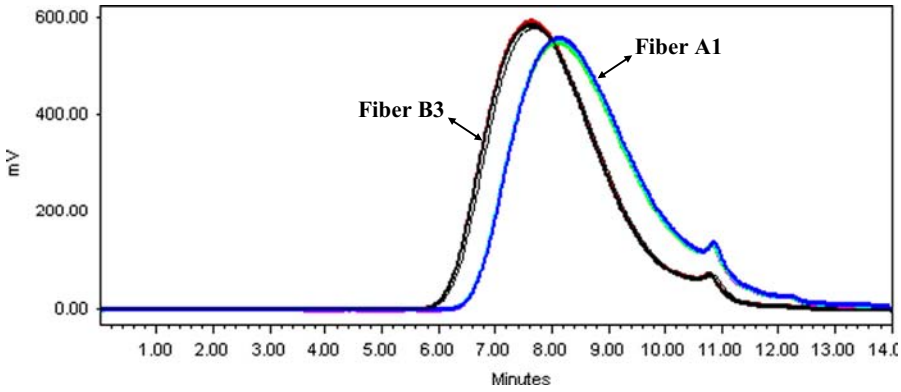

Fig. 9. Reproducibility of chromatograms of triplicates of two different PET fibers (A1 and B3). The calculated molecular weights are given in Table 2. GPC conditions are same as in Fig. 7.

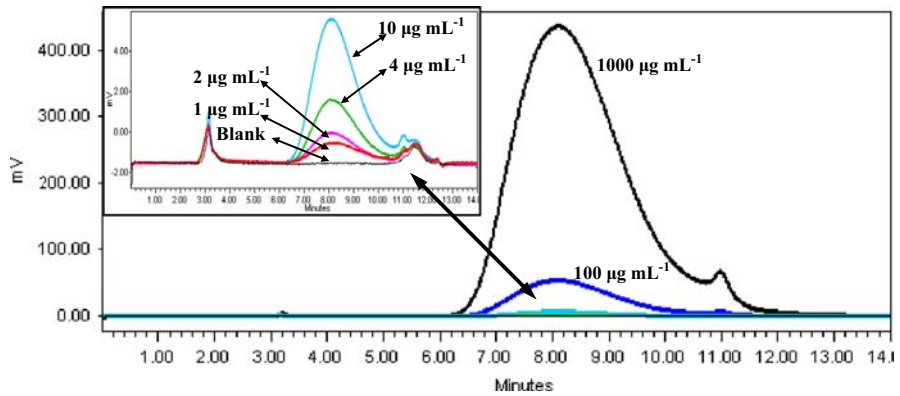

Fig. 10. GPC chromatograms for PET fibers at a concentration range of 1000–1 μg mL^{-1}. Calculated molecular weights are given in Table 3. GPC conditions are same as in Fig. 7.

Acknowledgment

The authors like to thank Dr. Georg Jochem and Stefan Deck of the Forensic Science Institute, Fiber section, Bundeskriminalamt, Wiesbaden, Germany for the assortment and microscopical examination of the fiber samples. Their help and advice is gratefully acknowledged.

References

[1] W. Steinmann, B. Glauss, S. Walter, J. Wulfhrost, G. Seide, T. Gries, Chem. Fibers Int. 62 (2012) 95–97.
[2] A. Kocak, The role of vibrational spectroscopy in forensic chemistry, in: L. Kobilinsky (Ed.), In Forensic Chemistry Handbook, 2012, pp. 251–267.
[3] P.M. Fredericks, in: J.M. Chalmers, H.G. M. Edwards, M.D. Hargreaves (Eds.), Forensic analysis of fibers by vibrational spectroscopy in Infrared and Raman Spectroscopy in Forensic Science, 2012, pp. 153–169.
[4] K. De Wael, L. Lepot, Sci. Justice 52 (2012) 161–167 (and 249-258).
[5] R. Palmer, The forensic examination of fibres, in: N.N. Daeid, M.M. Houck (Eds.), In Interpol's Forensic Science Review, 2010, pp. 2–18.
[6] K.R. Beck, D. Hinks, A. Crawford, N. Weisner, AATCC Rev. 12 (2012) 60–65.
[7] G. Montaudo, M.S. Montaudo, C. Puglisi, F. Samperi, Anal Chem. 66 (1994) 4366–4369.
[8] K. Wisskopfw, J. Polym. Sci. Polym. Chem. 26 (1988) 1919–1935.
[9] E.E. Drott, in: J. Cazes (Ed.), Liquid Chromatography of Polymers and Related Materials, Chromatographic Science Series, 8, Dekker, New York, 1976.
[10] S. Berkowitz, J. Appl. Polym. Sci. 29 (1984) 4353–4361.
[11] W.W. McGee, K. Coraine, J. Strimaitis, J. Liquid Chrom. 2 (1979) 287–299.
[12] K. Kretschmer, Krim. und Forens. Wiss. 75 (1989) 7–40.
[13] V. Causin, Anal. Methods 2 (2010) 792–804.
[14] G. Jochem, S. Deck, Personal communications 2011–2012.
[15] O. Heuse, F.P. Adolf, J. For. Sci. Soc. 22 (1982) 103–122.
[16] J.D. Badia, E. Stromberg, A. Ribes-Greus, S. Karlsson, Anal. Chim. Acta. 692 (2011) 85–95.