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CHARACTERIZATION AND IDENTIFICATION OF POLYAMIDE FIBRES BY INFRARED SPECTROMETRIC METHOD

According to the recommendation 2076—1973 of the International Standardization Organization (ISO), polyamide fibres are such chemical fibres whose polymer consists of linear (aliphatic) macromolecules with a periodically occurring —CO—NH-group in the chain. This standard has been supplemented with a concept, polyaramide, marking such chemical fibres whose polymer is an aromatic long-chain polyamide where at least 85% of the amido groups are directly bound to two aromatic nuclei, up to 60% of amido groups being possibly replaced by the aromatic imido groups [1]. The world industrial output of polyamide fibres comprises more than five hundred trade names.

As seen from Table 1, beginning with PA 3 to PA 12, the percentage of carbon increases from 60.86 up to 73.31%, while that of nitrogen falls from 11.24 to 6.82%, and hydrogen increases from 9.77 to 11.41%. The percentage of carbon in the Qiana alicyclic polyamide fibre is almost identical with that of PA 12 as well as those of nitrogen and hydrogen.

Elemental analysis was performed on a Hewlett-Packard analyzer model 185 (analyst R. Soosalu). Polyamides are synthesized from various monomers of different chemical structure, a member of polyamide fibres, such as PA 3, PA 4, PA 6, PA 7, PA 8, PA 9, PA 11, PA 12, PA 6.6 and PA 6.10 being prepared from the polymers obtained. The abbreviation «PA» means polyamide, the number is the carbon atom number in a polymer structural unit. The characterization and identification of the above fibres is rather complicated from the viewpoint of polymer analysis, but the problem requires a solution. Several attempts have been made to analyze organic and inorganic solvent

Table 1

Elemental analysis of some investigated polyamide fibres, %

Trade name	Proveniance	Type of fibre	C	H	N
Helanca	Netherlands	PA 3	60.86	9.77	11.24
Kapron	USSR	PA 6	63.27	9.83	11.61
Anid	USSR	PA 6.6	65.07	10.12	12.40
Oenanth	USSR	PA 7	65.84	10.23	10.72
Polyamide	GFR	PA 7	65.79	10.40	10.74
Rilsan	France	PA 11	73.29	11.17	7.56
Undecane	USSR	PA 11	71.81	11.20	7.42
Grilamid	Switzerland	PA 12	73.31	11.41	6.82
Qiana	U.S.A.	Alicycl. PA	72.66	10.67	6.59
Nomex	U.S.A.	Arom. PA	69.24	4.18	11.29
Fenilon	USSR	Arom. PA	69.39	4.22	—

Note: O_2 is estimated from the difference.

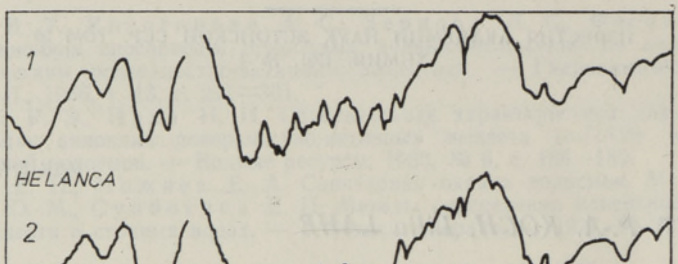


Fig. 1a. The infrared spectra of some polyamide fibres: 1 — Helanca; 2 — Kapron; 3 — Anid; 4 — Oenanth; 5 — Undecane.

Table 2

Melting points of polyamide fibres [4], °C

Polyamide 3	340
Polyamide 4	256
Polyamide 6	215
Polyamide 7	225
Polyamide 8	200
Polyamide 9	210
Polyamide 11	190
Polyamide 12	180
Polyamide 6.6	255
Polyamide 6.10	214
Alicyclic PA Qiana	275
Aromatic PA Nomex *	370
Aromatic PA Kevlar *	410

* decomposes

solubility of polymer fibres by different chemical methods [1]. Pyrolysis-mass spectrometry has been also used to characterize textile fibres [2]. Pyrolysis-gas chromatography has made it possible to qualitatively differentiate between PA 3, PA 6, Pa 6.2, PA 7, PA 11, PA 12 and the aromatic polyamide fibre Nomex [3].

The aim of this work was to find the possibilities of characterizing various polyamide fibres of different chemical structure and physico-chemical properties (aliphatic, alicyclic and aromatic) using the infrared spectrometric method as well as elemental analysis and data on the melting points. As polyamide fibres are industrial polymers manufactured in different chemical works under different production conditions, the melting points of fibres of the same type may differ within several degrees (Table 2). A heated-plate microscope may be used to determine the melting points. Infrared spectra were taken on a UR-10 using KBr pellet method. They are shown in Fig. 1.

The absorption bands of infrared spectra of the above polyamide

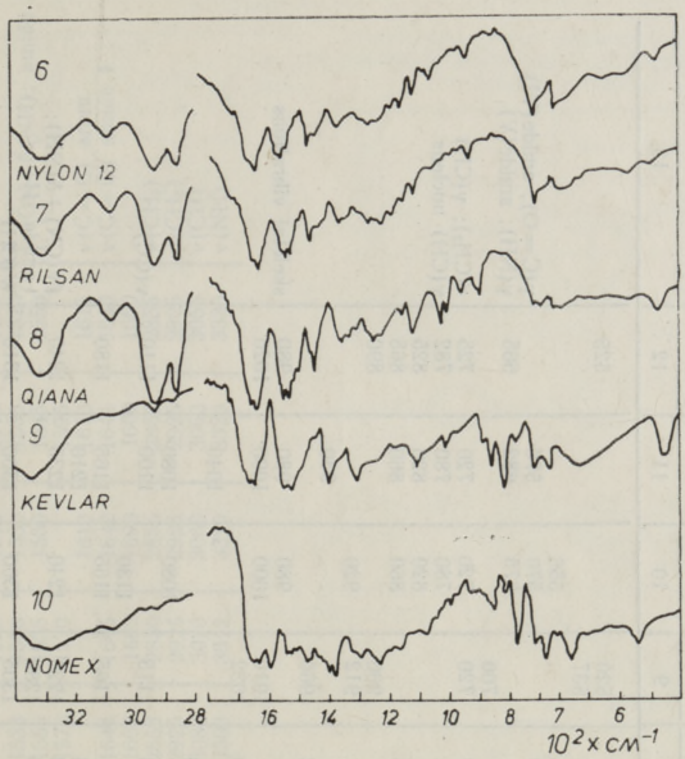


Fig. 1b. The infrared spectra of some polyamide fibres: 6 — Nylon 12; 7 — Rilsan; 8 — Qiana; 9 — Kevlar; 10 — Nomex.

fibres (aliphatic, alicyclic, and aromatic) and their interpretation are given in Table 3. More specific absorption bands are presented in Tables 4 and 5. The absorption bands of infrared spectra of polyamides are due to the vibrations of polymer chain forming CH_2- and strongly polar NH-groups. The stretching vibration of the NH-group of an aliphatic polyamide may be expressed by wave number 3300 cm^{-1}, that of C=0 (amide band I) by 1640 cm^{-1}, coupled vibration (amide band II) by 1500—1555 cm^{-1}. This is valid for the aliphatic and alicyclic polyamides. In the case of aromatic polyamides the vibrations of the benzene ring and C=C are added. In the case of aromatic polyamides the vibration frequencies of the NH-group are greater. Table 6 presents data on the vibration frequencies of secondary amido groups taken from [5] and obtained by the authors.

The structural units of alicyclic polyamide fibre Qiana and aromatic polyamide fibres (Nomex and Kevlar) are given in the form of schemes taken from [2].

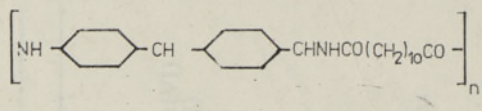
A structural unit of Qiana contains two hexyl groups in addition to the NH-, CH_2- and CO-groups. In the infrared spectrum of Qiana two absorption bands occur in the regions of 700 and 900 cm^{-1} not met with in a spectrum of any other polyamide fibre. Nomex and Kevlar are of a very similar chemical structure: Nomex is a poly(meta-phenylene isophthalamide), Kevlar — poly(para-phenylene terephthalamide). The differentiation between them on the basis of different intensities of fragment ions of mass spectra is possible but very complicated [2].

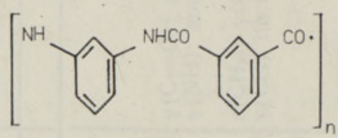
Table 3

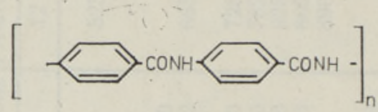
Absorption bands of infrared spectra of aliphatic and aromatic polyamide fibres, cm^{-1}

Helanca PA 3	Kapron PA 6	Anid PA 6.6	Oenanth PA 7	Undecane PA 11	Rilsan PA 11	Grilamid PA 12	Nylon PA 12	Qiana	Nomex PA-arom.	Fenilon PA-arom.	Kevlar PA-arom.	Assignment
1	2	3	4	5	6	7	8	9	10	11	12	13
	520							520			525	
532				540	545	535	537	537				
									556			
580	577	577	577	577	580		580		570	570		γ(C=O); amide(VI)
690	685	689	685						675	682	665	γ(NH); amide(V)
								700				
730	730	725	725	725	720	720	720	720	720	720	725	$r(CH_2)$; γ(CH)
									780	780	782	γ(CH) nucleus
				830					820	820	825	
							855		860	860	865	
								900			890	
								912	920			
934	930	935	937	928	938					930		
	960			960		945	948	960				
									980	980	980	skeletal vibrations
								1010	1000	1000	1020	
	1030			1030			1030	1032				
		1040								1040		
1040—65	1075	1064			1060	1065	1068					
			1080						1080	1080		
	1120		1124	1120	1124	1122	1124	1115		1100	1110	ν(CC)
1140		1140							1130			
1180	1170	1180	1165	1170	1160	1160	1161	1165	1165	1165	1180	
1200	1200	1197	1196	1200	1190	1190	1194			1210		
	1240	1225	1225	1228	1225	1230	1223	1225	1240	1235	1240	{ν(CN)+δ(NH);
1275	1265	1270	1270	1265	1280	1270	1270	1280				amide III
								1305	1300	1300	1310	W(CH)
			1358		1330—50			1336	1325	1325		
1370	1370	1370		1370	1370	1372	1370	1360	1380	1380		
									1410	1410	1403	
1418—55	1420—50	1420—50	1420—50	1420—50	1420—60	1440—60	1445—55	1450	1430	1420	1450	$\gamma(CH_2)$
1465	1465	1473	1465	1465	1470	1470	1470	1465	1470	1460—75	1465	$\delta(CH_2)$
1480	1480		1480	1480					1480	1495	1485	γ(CH)

1	2	3	4	5	6	7	8	9	10	11	12	13
	1505	1505	1505	1503				1505	1505			
	1517	1515	1517	1515				1520	1515	1515	1510	
1535	1530—40	1538	1536	1530	1537	1535	1538	1538	1530	1535	1520	{ν(CN+δ(NH); amide II
1553	1552	1552	1550	1550	1552	1555	1555	1555	1550	1545	1550	
1570	1570	1570	1570	1570	1570	1570	1570	1570		1595		
									1610	1610	1615	ν(C=C) arom.
1645	1635	1635	1635	1635	1644	1644	1644	1645	1642	1644	1640	ν(C=O) amide I
1662	1665	1660	1660	1660	1660	1665	1662	1662	1660	1660	1660	
2860	2855	2855	2850	2845	2850	2850	2853	2850	2855	2850	2855	ν(CH_2)
2930	2930	2930	2930	2930	2925	2925	2925	2925	2925	2925	2925	ν(CH_2)
3080	3080	3080	3080	3080	3080	3080	3080	3070	3060	3060	3055	ν(CH)
3300	3300	3300	3300	3300	3300	3300	3300	3312	3320	3320	3335	ν(NH)

Qiana —


Nomex —


Kevlar —


From Table 3 it can be seen that infrared spectra of polyamide fibres contain a lot of absorption bands (more than 30) which are difficult to interpret. Absorption bands presented in Table 4 were chosen for detailed characterization. From the Table it can be seen that the infrared spectra of aliphatic, alicyclic and aromatic polyamides contain a number of nearly coinciding absorption bands, such as 3300, 1635, 1645, 1530, 1535, 1465—1473, 1265—1280, 1165—1180, 720—735, 675—690, and 570—580 cm^{-1}. Increase in the number of CH_2-groups and decrease in that of NH-groups in a linear polymer chain of aliphatic polyamides brings along a weakening of the absorption band of amide V (690 cm^{-1}) and amide VI (570—580 cm^{-1}), so that it is practically impossible to measure these bands in the case of PA 11, PA 12 and alicyclic polyamide.

Table 5 gives the absorption bands which are typical of only aromatic polyamides such as Nomex, Fenilon and Kevlar. The vibration frequencies of the NH-group in the infrared spectra of aromatic polyamide are different in the case of Nomex; Fenilon has 3320, Kevlar 3335 cm^{-1}, the C=C vibration is also different, being 1610 cm^{-1} in the case of Nomex and Fenilon, 1615, 1410 and 1403 cm^{-1} in the case of Kevlar. Unlike Nomex and Fenilon, the absorption band 570 cm^{-1} in the infrared spectrum of Kevlar (see amide band VI) is absent. (NH) amide band V in the infrared spectrum of Kevlar is 665, being 675 and 682 cm^{-1} in the case of Nomex and Fenilon, respectively.

In conclusion it may be said that aliphatic, alicyclic and aromatic polyamide fibres may be characterized on the basis of their infrared spectra and corresponding absorption bands. More detailed identifi-

Table 4

Type of fibre	Absorption bands of polyamide fibres, cm^{-1}								
Aliphatic:									
PA 3	3300	1645	1535	1465	1275	1180	730	690	580
PA 6	3300	1635	1535	1465	1265	1170	730	689	577
PA 7	3300	1635	1536	1465	1270	1166	725	685	577
PA 11	3300	1635	1530	1470	1278	1170	725		577
PA 11	3300	1644	1537	1470	1280	1160	720		
PA 12	3300	1644	1535	1470	1270	1160	720		
PA 12	3300	1644	1535	1470	1270	1161	720		
PA 66	3300	1635	1538	1473	1270	1180	720	689	577
PA alicycl.	3312	1645	1538	1465	1280	1165	720		
Aromatic:									
PA Nomex	3320	1642	1530	1470	1240	1165	720	675	570
PA Fenilon	3320	1644	1535	1468	1235	1165	720	682	570
PA Kevlar	3335	1640	1535	1465	1240	1180	725	665	

Table 5

Type of fibre	Absorption bands of aromatic polyamide fibres only, cm⁻¹			
PA Nomex	1610	1410	980	780
PA Fenilon	1610	1410	980	780
PA Kevlar	1615	1403	980	782

Table 6

Approximate wave numbers (cm^{-1}) of the vibrations of secondary groups of aliphatic polyamides

Amide band	Assignment	Wave numbers by	
		Hummel	Kirret et al.
I	(C=O)	1640	1640
II	(C—N)+(NH)	1550	1553
III	(C—N)+(NH)	1280...50	1280...65
IV	(C=O)	not identified	
V	(NH)	700	687
VI	(C=O)	600	578

cations are possible but in addition to infrared spectra other analytical indices such as fibre elemental analysis and melting points should also be used.

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POLÜAMIIDKIUDUDE ISELOOMUSTAMINE NING IDENTIFITSEERIMINE INFRAPUNASE SPEKTROMEETRIA ABIL

Artiklis käsitletud alifaatsete, alitsükliliste ja aromaatsete polüamiidkiudude infrapunaste spektrite absorptsiooniribad on paljudel juhtudel sarnased, kuid neis on ka spetsiifilisi erinevusi, mis võimaldab neid eristada. Kiudude identifitseerimisel tuleb arvesse võtta ka elemendianalüüsi andmeid ja sulamistäppi.

О. КИРРЕТ, П.-А. КОХ, Лилья ЛАХЕ

ХАРАКТЕРИСТИКА И ИДЕНТИФИКАЦИЯ ПОЛИАМИДНЫХ ВОЛОКОН МЕТОДОМ ИК-СПЕКТРОСКОПИИ

В статье рассмотрены полосы поглощения инфракрасных спектров разных полиамидных (алифатических, алициклических и ароматических) волокон. Найдено, что во многих случаях имеются совпадающие полосы поглощения, а наряду с ними и ряд специфических, свойственных отдельным типам волокон. В случае идентификации отдельных типов волокон рекомендуется учитывать данные элементного анализа и температуру плавления.