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## CHARACTERIZATION AND IDENTIFICATION OF POLYACRYLONITRILE FIBRES AND THEIR MODIFICATIONS AND MODACRYLIC FIBRES BY INFRARED SPECTROMETRIC METHOD

Polyacrylonitrile fibres, often shortly called polyacrylic fibres, are known under several hundred trade names. The world output of synthetic polyacrylic fibres has attained the third place after polyester and polyamide fibres.

According to the recommendation 2076 1973 of the International Standardization Organization (ISO), polyacrylic fibres are synthetic fibres formed from such high polymers which have been linearly polymerized from at least 85% of vinyl cyanide/acrylonitrile [1]. Modacrylic fibres are synthetic fibres formed by linear polymerization from less than 85 wt. %, but more than 50 wt. % of acrylonitrile. In the ISO's recommendation 2076/DAM 2 the lower limit is terminologically incorrectly fixed, it being at least 35 wt. % of acrylonitrile. Acrylonitrile is subjected to emulsion (suspension) or solvent polymerization in the redox system in aqueous ammonium peroxydisulfate solution (1:10) in the presence of sodium hydrogen sulfate or sodium thiosulfate as catalysts with an average molecular mass of 60 000 to 100 000 (the chain containing 1200 or 2000 basic molecules, respectively) [2, 3].

The pure polyacrylic fibres thus obtained are used as technical fibres and together with viscose fibres also in manufacturing carbon fibres. In order to gain better textile-technological properties and fibre dyeing, pure acrylonitrile is not polymerized alone, but appropriate unsaturated monomers such as vinyl acetate, vinyl pyridine, methyl methacrylate and acrylamide are added, which at polymerization break the polyacrylonitrile structure, thus promoting the absorption of dyes into the polymer, or alkaline groups are added which permit the use of acid dyes by dyeing [4].

As the amounts of additives in the polymers modified this way are lower than 15%, then according to the definition such polymer fibres belong to polyacrylonitrile fibres. Most of them contain 89—95% of polymerized acrylonitrile and 5—11% of some comonomer, i. e., an acetate, sulfo- or sulfonate group [5] or some other groups. The wide use of polyacrylic fibres for manufacturing textile fabrics and carpets suggested the need for improving their flameproof properties. Most of the acrylic fibres used nowadays are made more flameproof by introducing high amounts of halogen-containing components into the polymer. Such fibres are called modacrylic or also multipolymerizate fibres. As comonomers, vinyl chloride or vinylidene chloride are used, 35—50% of them being polymerized into a polymer.

In this work, two modacrylic fibres (Dynel and Verel 17) were subjected to investigation. Their elemental analysis is given in Table 1, and absorption bands of infrared spectra in Table 2. As comonomers, various chemical compounds are used, such as vinyl pyrrolidone, alkyl



Table 1

Elemental analysis of some investigated polyacrylonitrile fibres, %

Fibres		C	H	N	C+H+N
Trade name	Provenience				
Polyacrylic					
Acribel	Belgium	66.90	5.93	24.50	97.33
Acrilan	USA	65.61	5.48	23.41	94.50
Cashmilon	Japan	66.09	5.83	24.71	96.63
Creslan	USA	67.00	5.73	25.44	98.17
Crylor	France	67.19	5.81	24.86	97.86
Dolan	GFR	66.95	6.00	24.58	97.53
Dralon	GFR	65.90	5.84	24.37	96.11
Exlan L	Japan	66.09	5.74	23.71	95.54
Exlan S	Japan	67.61	5.70	23.62	96.93
Nitron	USSR	67.61	5.69	25.36	98.66
Prelana	GDR	67.06	5.77	25.89	98.72
Tacryl A	Sweden	66.44	5.78	24.45	96.67
Vonnel	Japan	66.48	5.85	23.61	95.94
Zefran	USA	67.14	5.83	25.01	97.98
Modacrylic					
Dynel	USA	53.26	5.71	10.65	69.58
Verel 17	USA	49.98	5.02	13.01	68.01

vinyl sulfone, styrene sulfonic acid, vinyl phosphonic acid, polymerizing dicarboxylic acid, etc. [5]. The minute amounts of compounds in polyacrylonitrile copolymers are rather difficult to identify by the spectroscopic method [5].

From Table 1 it is evident that by elemental analysis on a Hewlett-Packard model 115 analyzer, the sum of C, H and N does not amount to 100%, the difference being caused by oxygen, sulfur and chlorine contained in comonomers (modacrylic fibres) and by a flattening agent. Polyacrylonitrile fibre Dralon was found to contain 0.39% sulfur and about 0.3—0.5%  $\text{TiO}_2$  as flattening agent [6].

The infrared spectra of pure polyacrylic fibres (100% grade) have been investigated earlier by several authors, the works of Yamadera's group [7] arousing special interest. His work has also been used as a basis in this investigation at the interpretation of absorption bands of spectra of modified polyacrylonitrile and modacrylic fibres.

The goal of this work is to elucidate to what extent infrared spectrometry can be used to characterize and identify modified polyacrylic and modacrylic fibres. This is rather complicated because trace amounts of tens of different compounds must be detected in acrylonitrile copolymers. The authors have also dealt with the identification of individual polyacrylic (modified) and modacrylic fibres produced under various trade names, using either the pyrolysis gas chromatographic [8] or microscopic method for distinguishing fibres of different cross-sections [9].

Table 2 presents the absorption bands of infrared spectra of pure polyacrylic, polyacrylic and modacrylic fibres of different origin. Data of Yamadera et al. (taken from [5]) about pure polyacrylonitrile have been used for interpretation, but similarly to the modified polyacrylonitrile fibres, a large number of monomers polymerized into the main polymer in low concentrations only, must be dealt with, and therefore spectral data were taken from the literature.

Chemical fibres of this type are characterized and identified on the



Table 2

Absorption bands of infrared spectra of polyacrylonitrile fibres, their modifications and modacryl fibres

Acritel	Acrilan	Bulana	Cashmilon	Creslan	Crylor	Dolan	Dralon	Exlan L	Exlan S	Nitron	Prelana	Tacryl A	Vonnel	Zelran	Dynel	Verel 17	Assignment [5]
535	538	535	535	538	535	535	538	535	538	535	535	535	538	535	535	535	$\sigma$ (C—C—CN)
—	605	—	—	605	—	—	—	—	605	—	—	—	610	—	625	650	$\nu$ (C—Cl)
—	645	—	—	645	—	—	—	—	735	—	—	—	735	—	694	—	$\nu$ (C—CN); $\nu$ (CH <sub>2</sub> )
770	735	770	770	770	770	765	770	765	770	765	770	770	770	770	780	840	
—	835	—	—	835	—	—	—	835	835	955	—	—	835	—	840	—	
—	940	—	—	940	—	—	—	955	1030	—	—	—	940	—	—	—	
1040	1025	1040	—	1030	1040	1040	—	1072	1075	1075	1075	1075	1030	1070	1020	—	$\nu$ (CC); $\nu$ (CH <sub>2</sub> )
1075	1075	1072	1070	1075	1070	1076	1075	—	—	—	—	—	1075	—	1100	1130	
1128	1128	1128	—	—	1125	—	1172	1170	—	—	—	1170	—	1170	1208	1170	$\omega$
1170	1180	1170	1170	1180	1180	1170	1225	1225	1235	1240	1240	1238	1235	1230—40	1250	1230	$\omega$ (CH); $\omega$ (CH <sub>2</sub> ); $\nu_a$ (CC)
1233	1235	1233	1225—45	1235	1233	1223	—	—	—	—	—	—	—	—	—	—	$\sigma$ (CH); $\omega$ (CH <sub>2</sub> ); $\nu_a$ (CH)
—	1300	—	—	1300	—	—	—	—	1300	1315	—	—	1300	1290	—	—	$\nu$ (CC)
1355	1355	1360	1355	—	1355	1355	1360	1360	1360	1355	1355	1355	1365	1360	1355	1365	
1365	1365	—	1365	1367	1365	1365	1367	1368	—	1365	1365	—	1400	—	—	—	
—	1400	—	1410	—	—	—	—	—	1400	—	—	—	1450	—	—	1382	
1450	1450	1450	1450	1450	1451	1450	1458	1450	1450	1450	1450	1450	1450	1450	1440	1445	$\sigma$ (CH <sub>2</sub> )
—	1490	—	—	1490	—	—	—	—	1490	—	—	—	1490	—	—	1500	
—	—	—	—	1565	—	—	—	—	1558	—	—	—	1600	—	—	1512	
—	1600	—	1610	1600	—	1634	—	1634	1600	1634	—	1634	1630—40	—	1530	1530	
—	1625	1612	—	—	—	—	—	—	—	—	—	—	1630	—	1630	1547	amide II
1670	1678	1675	1678	—	1664	—	1670	1735	—	1725	—	1727	—	1680	—	1562	
1725	1730	1725	1725	1735	1722	1728	1735	1735	1735	1725	1725	1727	—	—	—	1640	amide I
2242	2242	2242	2241	2241	2242	2244	2243	2241	2242	2244	2244	2244	1735	—	1725	1666	
2870	2870	2868	2870	2870	2865	2868	2835—70	2868	2870	2870	2870	2865	1715	—	1715	1715	$\nu$ (C=O)
2930	2930	2930	2935	2935	2935	2930	2930	2935	2935	2930	2930	2930	2240	2240	2240	2240	$\nu$ (C $\equiv$ N)
—	—	—	—	—	—	—	—	—	—	—	—	—	2870	2870	2860	2860	$\nu_s$ (CH <sub>2</sub> )
—	—	—	—	—	—	—	—	—	—	—	—	—	2930	2935	2920	2925	$\nu$ (CH)
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2952	2965	$\nu_a$ (CH <sub>2</sub> )



Table 3  
More characteristic absorption bands  
of polyacrylonitrile fibres,  $\text{cm}^{-1}$

Pure polyacrylonitrile (measured by Yamadera et al. [5])	Relative intensity *	Modified polyacrylonitrile (measured by authors) (average)
2950	vs	—
2930	sh	2930
2870	m	2867
2237	vs	2242
	vs	1729
	m	1673
1447	vs	1449
1362	m	1362
1355	—	—
1247	m	1234
1073	st	1073
778	m	769
537	m	536

\* vs — very strong sh — shoulder, st — strong, m — middle.

bands in the same region, which belong to the polymerized monomers. The interpretation of absorption bands in the above region is the basic problem in this work.

According to the data of Yamadera et al. [5], the absorption bands in the infrared spectrum of pure polyacrylonitrile occur in the region 2950 and  $2930\text{ cm}^{-1}$ . The absorption band  $2950\text{ cm}^{-1}$  is absent in the infrared spectra of pure polyacrylonitrile identified by Hummel [10] and in those of modified polyacrylic fibres identified by Kirret et al. [8], but the absorption band  $2930\text{ cm}^{-1}$  is present. On the other hand, the infrared spectrum of modacrylic fibres, such as Dynel, contains two absorption bands, 2920 and  $2952\text{ cm}^{-1}$ , Verel 17 has also two absorption bands, 2925 and  $2965\text{ cm}^{-1}$ .

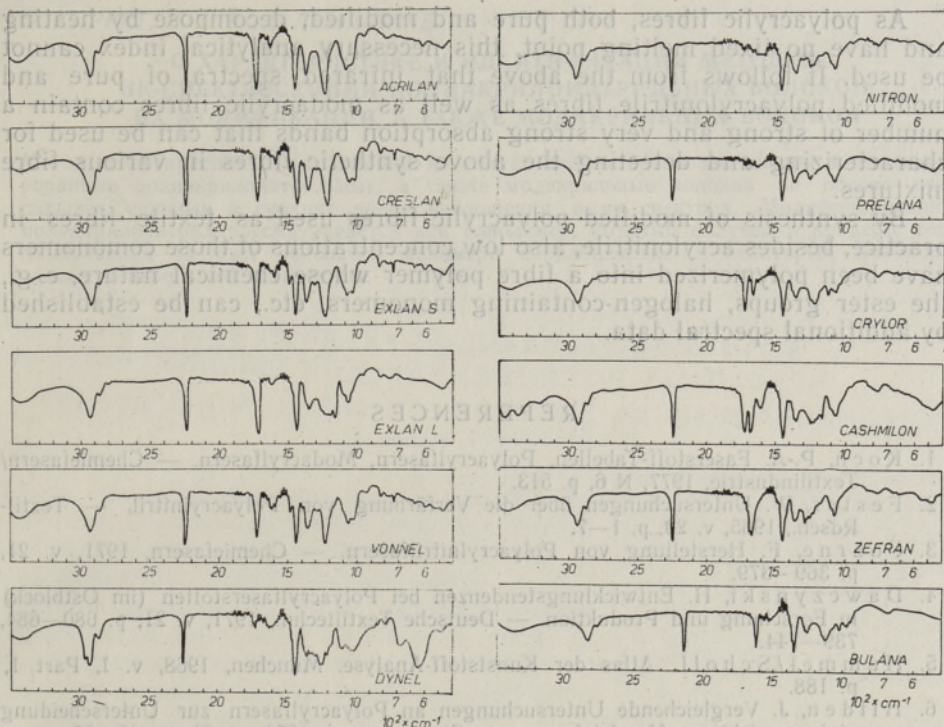
In 14 cases (Figure), the infrared spectra of modified polyacrylonitrile contain a very strong absorption band in the region  $1722\text{--}1735\text{ cm}^{-1}$  (average  $1729\text{ cm}^{-1}$ ) which is characteristic of the ester group  $\nu(\text{C}=\text{O})$  vibration, more precisely, of the carboxylic group  $(\text{C}=\text{O})$  vibration. In the literature, the absorption bands  $1729\text{ cm}^{-1}$  (average),  $1362\text{ cm}^{-1}$  (average) and  $1228\text{ cm}^{-1}$  (average) are correlated with the acetate structure [11], correspondingly with the  $\nu(\text{C}=\text{O})$  stretching vibration.

Difficulties arise when, besides vinyl acetate, also methacrylic acid and its derivatives are used as comonomers whose molecules contain the carboxylic,  $-\text{CH}_3$  and  $-\text{COC}$  groups, and the absorption bands of their infrared spectra coincide with those of the acetate structure. The differentiation between the above structures by the conventional infrared spectrometric method is practically impossible, suggesting the need for the spectroscopic or some other method. As seen from Table 2, the  $\delta(\text{CH})$  vibration  $1362\text{ cm}^{-1}$ ,  $\omega(\text{CH}_2)$  vibration  $1247\text{ cm}^{-1}$  and a weak vibration  $1227\text{ cm}^{-1}$  are present in the infrared spectrum of pure polyacrylonitrile; thus, this phenomenon is not specific of the ester groups only. The absorption bands 1670, 1677, 1675, 1666 and  $1683\text{ cm}^{-1}$  are amide bands I, 1558, 1565 and  $1562\text{ cm}^{-1}$  amide bands II. The interpretation of

basis of the infrared spectrum of pure polyacrylonitrile. In order to characterize pure polyacrylonitrile, only two strong absorption bands will suffice. It was found that the  $\text{C}\equiv\text{N}$  vibration in the side chain of a polymer is  $2242\text{ cm}^{-1}$  (average of 17 determinations) and the  $\text{CH}_2$  vibration of the main chain  $1450\text{ cm}^{-1}$  (average of 17 determinations) by using the KBr pellet method.

To characterize and possibly identify low amounts of comonomers in the polyacrylic copolymer, only strong and very strong absorption bands of infrared spectra were chosen (Table 3). On the grounds of these absorption bands, the chemical nature of comonomers polymerized into a polymer can be elucidated. In the infrared spectrum of pure polyacrylonitrile the absorption bands in the region 1447 and  $2183\text{ cm}^{-1}$  are absent. The infrared spectra of modified polyacrylonitrile and modacrylic fibres contain a lot of absorption

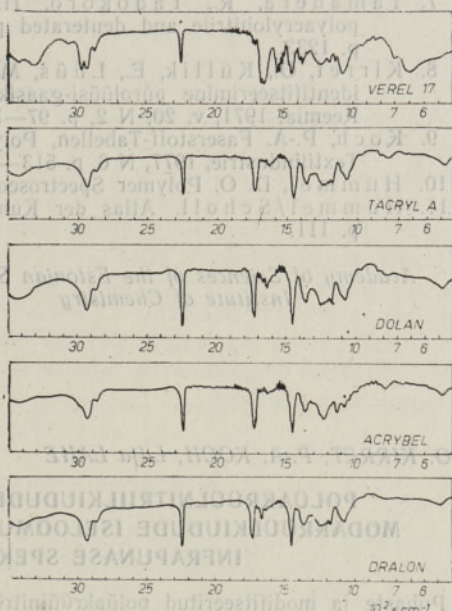




The infrared spectra of some polyacrylonitrile fibres.

absorption bands of other modified polyacrylonitrile fibres is presented in detail in Table 2. It may be said that the infrared spectra of several modified polyacrylic fibres (Acrilan, Creslan, Vonnell and Exlan S) are in general very similar, containing probably methacrylate as comonomer. Zefran contains presumably vinyl pyrrolidone as comonomer.

The infrared spectra of modified acrylic fibres show that Verel 17 contains an absorption band  $650\text{ cm}^{-1}$  that corresponds to the C-Cl vibration of polyvinylidene chloride. Elemental analysis showed this fibre to contain more than 30 wt. % of chlorine. The infrared spectrum of Verel 17 has no  $\nu(\text{C}=\text{O})$  vibration corresponding to the ester group. The amide structure is proved by an amide band I (NH)  $1640\text{ cm}^{-1}$  and amide band II (C-N) (NH)  $1547\text{ cm}^{-1}$ . Obviously this is a monosubstituted methacrylamide. The absorption bands  $\gamma(\text{C}=\text{O})$   $1725\text{ cm}^{-1}$ ,  $\delta(\text{CH}_3)$   $1355\text{ cm}^{-1}$ , (COC)  $1250\text{ cm}^{-1}$ , typical of the ester group, are present in the infrared spectrum of Dynel. The infrared spectrum of Dynel contains absorption bands 625 and  $694\text{ cm}^{-1}$  corresponding to the C-Cl vibrations of polyvinyl chloride.





As polyacrylic fibres, both pure and modified, decompose by heating and have no fixed melting point, this necessary analytical index cannot be used. It follows from the above that infrared spectra of pure and modified polyacrylonitrile fibres as well as modacrylic fibres contain a number of strong and very strong absorption bands that can be used for characterizing and detecting the above synthetic fibres in various fibre mixtures.

By synthesis of modified polyacrylic fibres used as textile fibres in practice, besides acrylonitrile, also low concentrations of those comonomers have been polymerized into a fibre polymer whose chemical nature, e. g., the ester groups, halogen-containing monomers, etc., can be established by additional spectral data.

## REFERENCES

1. Koch, P.-A. Faserstoff-Tabellen, Polyacrylfasern, Modacrylfasern. — *Chemiefasern/Textilindustrie*, 1977, N 6, p. 513.
2. Fester, W. Untersuchungen über die Verfärbung von Polyacrylnitril. — *Textil-Rdsch.*, 1965, v. 20, p. 1—7.
3. Fourne, F. Herstellung von Polyacrylnitrilfasern. — *Chemiefasern*, 1971, v. 21, p. 369—379.
4. Dawczynski, H. Entwicklungstendenzen bei Polyacrylfaserstoffen (im Ostblock) in Forschung und Produktion. — *Deutsche Textiltechn.*, 1971, v. 21, p. 680—684, 739—744.
5. Hummel/Scholl. Atlas der Kunststoff-Analyse. München, 1968, v. I, Part 1, p. 188.
6. Hilden, J. Vergleichende Untersuchungen an Polyacrylfasern zur Unterscheidung einiger wichtiger Handelsfasern. — *Chemiefasern*, 1971, v. 21, p. 49—55.
7. Yamadera, R., Tadokoro, H., Murahashi, S. Normal vibrations of polyacrylonitrile and deuterated polyacrylonitriles. — *J. Physics*, 1964, v. 41, p. 1233.
8. Kirret, O., Küllik, E., Lüüs, M. Polüakrüülnitriil ja multipolümerisaatkiudude identifitseerimine pürolüüsi-gaasikromatograafia meetodil. — *ENSV TA Toim. Keemia*, 1971, v. 20, N 2, p. 97—100.
9. Koch, P.-A. Faserstoff-Tabellen, Polyacrylfasern, Modacrylfasern. — *Chemiefasern/Textilindustrie*, 1977, N 6, p. 513—524.
10. Hummel, D. O. *Polymer Spectroscopy*. Weinheim, 1974, p. 143.
11. Hummel/Scholl. Atlas der Kunststoff-Analyse. München, 1968, v. I, Part 1, p. 111.

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## POLÜAKRÜÜLNITRIILKIUDUDE, NENDE MODIFIKATSIOONIDE JA MODAKRÜÜLKIUDUDE ISELOOMUSTAMINE NING IDENTIFITSEERIMINE INFRAPUNASE SPEKTROMEETRIA MEETODIL

Puhaste ja modifitseeritud polüakrüülnitriilkiudude ning modakrüülnitriilkiudude iseloomustamiseks saab kasutada nende infrapunastes spektrites esinevaid väga tugevaid, tugevaid ja keskmise tugevusega absorptsiooniribasid.

Modifitseeritud polüakrüülnitriili tuleb vaadelda kui kopolümeeri, milles põhimonomeri akrüülnitriili kõrval on kopolümerisatsioonil kasutatud väiksemates kogustes ühte, kahte ja koguni kolme monomeeri; viimaste identifitseerimine on küllaltki komplitseeritud, kui kasutada ainult infrapunast spektromeetria.

# О ХАРАКТЕРИСТИКЕ И ИДЕНТИФИКАЦИИ МЕТОДОМ ИК-СПЕКТРОСКОПИИ ПОЛИАКРИЛОНИТРИЛЬНЫХ ВОЛОКОН, ИХ МОДИФИКАЦИЙ, А ТАКЖЕ МОДАКРИЛЬНЫХ ВОЛОКОН

Метод инфракрасной спектроскопии позволяет охарактеризовать чистые и модифицированные полиакрилонитрильные, а также модакрильные волокна на основе очень сильных, сильных и средних полос поглощения в их спектрах. Модифицированный полиакрилонитрил рассматривается как сополимер, который получен в процессе сополимеризации на базе основного мономера акрилонитрила и некоторых мономеров, взятых в небольшом количестве.

Содержание атмосферы воздуха, содержащего пары ароматических соединений, в основном, в акрилонитрильных волокнах, является важным фактором, влияющим на их свойства. В частности, наличие таких паров приводит к образованию в волокнах различных модификаций, которые могут быть идентифицированы с помощью инфракрасной спектроскопии.

В инфракрасном спектре акрилонитрила (AN) в области 2200 см<sup>-1</sup> наблюдается сильная полоса поглощения, соответствующая валентным колебаниям нитрильной группы. Эта полоса является основным признаком для идентификации AN в волокнах. Кроме того, в спектре AN наблюдаются и другие характерные полосы, такие как полосы в области 1400-1600 см<sup>-1</sup>, соответствующие колебаниям цикла. В модифицированных волокнах эти полосы могут изменяться, что указывает на наличие других химических групп в составе полимера.

В модифицированных волокнах, полученных в процессе сополимеризации AN с другими мономерами, в инфракрасном спектре наблюдаются дополнительные полосы поглощения. Например, в модифицированных волокнах, полученных в процессе сополимеризации AN с акрилонитрилом (AN-AN), в спектре наблюдаются дополнительные полосы в области 1400-1600 см<sup>-1</sup>, соответствующие колебаниям цикла. В модифицированных волокнах, полученных в процессе сополимеризации AN с акрилонитрилом (AN-AN), в спектре наблюдаются дополнительные полосы в области 1400-1600 см<sup>-1</sup>, соответствующие колебаниям цикла.

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