¹H-NMR Spectroscopic Investigation of Polyamide Fibers Grafted with Vinyl Monomers

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SYNOPSIS

Nuclear magnetic resonance spectroscopy was used to investigate the position of active centers in polyamide fibers subjected to graft copolymerization with poly(acrylic acid), poly(itaconic acid), and poly(2-vinylpyridine) initiated by thermal oxidation in air. As a result, structural changes in polyamide fibers brought about by oxidation and subsequent grafting of the above mentioned polymers were observed. It was estimated that the generation of active centers that initiate the copolymerization take place at the nitrogen atoms of the amide groups in the polyamide chain. This was confirmed by the broadening of the absorption band for the methylene group adjacent to the nitrogen as well as by the absence of a new absorption band for the methine groups, assuming that the generation of active centers and grafting would take place at the carbon atom of the methylene group in position α to the amide group. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Grafting vinyl monomers onto polyamide fabrics has been one of the methods for the chemical modification of these textiles.[1-9] Recently published articles on this subject concern fiber properties modified by grafting,[3,7,10-16] location and conformation of grafted chains,[17] and methods of initiating the grafting process.[1,2,7-12,18-30] Little reliable information, however, is available concerning the position where active sites are formed in polyamide chains due to initiation.

The simplest method of chemical activation of graft copolymerization consists of statistical addition of reactive groups (e.g., hydroperoxide and peroxide groups) to the polymer chain to form a polyfunctional initiator through the action of a redox system[2,5,9] or by direct oxidation of the polymer with atmospheric oxygen,[7,29,30] oxygen–ozone mixture, or ozone. These groups are decomposed at elevated temperatures (over 333 K) to produce oxygen polymer radicals. If the process is carried out in the presence of vinyl monomers, it results in graft copolymerization.

The determination of the position of active centers in the polyamide macromolecule is controversial.[31-37] Using thermal[29,30] or chemical initiation[33,34,38] in polyamide fibers, the active centers and consequently grafting can take place either at the nitrogen atom of the amide group[32,33,37,38] or at the carbon atom of the methylene group in the α position in relation to the amide nitrogen.[31,35,36] This question has not been answered yet, although numerous authors working on graft copolymerization have suggested one or another mechanism, neglecting experimental examination and quoting only vague opinions on the subject. Therefore, it was decided to take a closer look at this issue.

Of the analytical techniques suitable for this purpose, IR[38,39] and NMR spectroscopy seem to be both helpful and adequate. The latter method is one of the best instrumental techniques for structural and stereochemical examination of organic compounds, with the proton NMR spectra being the most common for this investigation.

The main objective of the present investigation is to determine the position of active centers in the polymer chain of polyamide fibers after thermal oxidation, and consequently to determine the site of grafting. Thus, in this study polyamide fibers oxi-

dized and grafted with various vinyl polymers were examined by ^{1}H-NMR spectroscopy.

EXPERIMENTAL

Materials

The following PA6 samples were used in this study: untreated fibers,[29] fibers oxidized in air at 393 K,[29] fibers grafted with poly(acrylic acid) (PAA) with the extent of grafting from 0.071 to 0.51% mol/g fiber,[30] fibers grafted with poly(itaconic acid) (PIA) with the extent of grafting from 0.013 to 0.026% mol/g fiber,[30] fibers grafted with poly(2-vinylpyridine) (PVP) with the extent of grafting from 0.01 to 0.036% mol/g fiber.[30]

The fiber samples were dissolved in deuterated sulfuric acid (D_2SO_4) with an addition of the internal standard tetramethylsilane (TMS). Because the D_2SO_4 solutions showed considerable viscosity, limited solubility, and contained suspended matters that undesirably affected the resolving power, formic acid was used as a solvent. As an external standard, TMS was applied. It was introduced into the samples in a sealed capillary placed precisely in the sample axis, because it was incompatible with the polyamide solution. The capillary was placed in a 5-mm diameter test tube. The test tubes were filled up to the level ensuring maximum sensitivity. They contained 50 mg of a PA6 fiber sample dissolved in 0.4 mL of formic or deuterated sulfuric acid. When the extent of grafting was high, a lower concentration of the polymer was used, that is, 10 mg of fibers grafted with PAA were dissolved in 0.4 mL of the solvent to avoid the formation of a dense gelatinous mass.

The ^{1}H-NMR spectra presented in this study were taken by means of a BS 487C NMR spectrometer from TESLA (Brno, Czechoslovakia) with a range of basic frequency of 80 MHz, provided with the recording and integrating devices. All ^{1}H-NMR spectra were obtained at 297 K using the frequency 1,000 Hz.

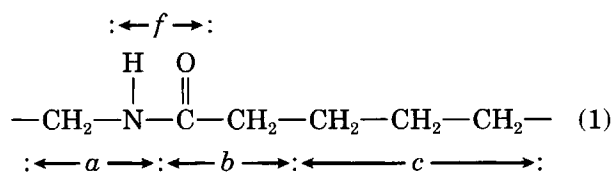### ^{1}H-NMR Spectra Examination Method

The appropriate values of chemical shifts were conformed to particular signals on the basis of the tables given by Zschunke[40] and the quantities of methylene proton shifts were taken from Schoolery and Dailey's list.[41,42] All the spectra were completed with integration curves. The integration curves are used to read off the heights of individual signals that are proportional to the surface area under the signal. In the presented ^{1}H-NMR spectra, the methylene group adjacent to the carbonyl group, designated below as b (formula 1), was assumed as the initial one.

RESULTS AND DISCUSSION

Graft copolymerization affects the polymer microstructure, particularly the chemical structure of the initial polymer due to the addition of another polymer to its main chain. Beside the characteristic atom arrangements in PA6, new bonds appear in the grafted polymer.

$$: \leftarrow f \rightarrow :$$
$$\begin{array}{cc} H & O \\ | & \| \end{array}$$
$$-CH_2-N-C-CH_2-CH_2-CH_2-CH_2- \quad (1)$$
$$: \leftarrow a \rightarrow : \leftarrow b \rightarrow : \leftarrow c \rightarrow :$$

The oxidation of polyamide with atmospheric oxygen at an elevated temperature and then its grafting with vinyl monomers result in new compounds of the following structures:

oxidation:

$$\begin{array}{c} -C-N-(CH_2)_5- \quad (2) \quad \text{or} \\ \| \quad | \\ O \quad OOH \end{array}$$

$$\begin{array}{c} -C-N-CH-(CH_2)_4- \quad (2') \\ \| \quad | \quad | \\ O \quad H \quad OOH \end{array}$$
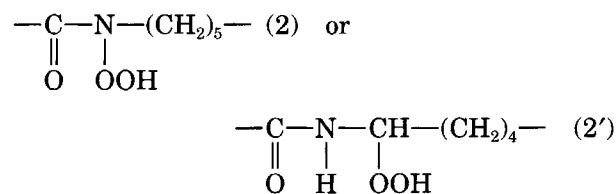
decomposition of hydroperoxide groups:

$$\begin{array}{c} -C-N-(CH_2-)_5- \quad (3) \quad \text{or} \\ \| \quad | \\ O \quad O° \end{array}$$

$$\begin{array}{c} -C-N-CH-(CH_2-)_4- \quad (3') \\ \| \quad | \quad | \\ O \quad H \quad O° \end{array}$$

grafted copolymers:

$$\begin{array}{c} -C-N-(CH_2-)_5- \quad (4) \quad \text{or} \\ \| \quad | \\ O \quad O-(X)_m \end{array}$$

$$\begin{array}{c} -C-N-CH-(CH_2-)_4- \quad (4') \\ \| \quad | \quad | \\ O \quad H \quad O-(X)_m \end{array}$$
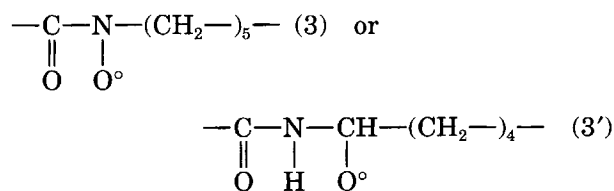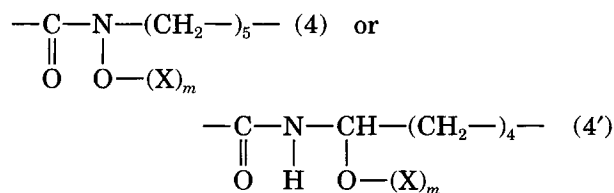
where X can be a polymer chain of PAA (5), PIA (6), or PVP (7) and m is polymerization degree of attached polymer.

$$-(-CH_2-CH-)_m-$$
$$|$$
$$COOH$$

(5)

$$COOH$$
$$|$$
$$-(-CH_2-C-)_m-$$
$$|$$
$$CH_2-COOH$$

(6)

$$-(-CH_2-CH-)_m-$$
$$|$$
$$C_5H_4N$$

(7)
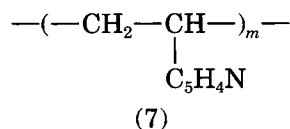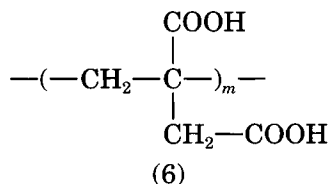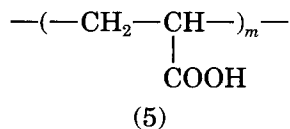
Interpretation of ^{1}H-NMR Spectra Recorded in D_2SO_4

The spectra of untreated and PAA grafted PA6 samples with the extent of grafting $x = 0.24\%$ mol/ g fiber are shown in Figures 1 and 2. These spectra reveal no impurity signals. Values of chemical shifts for individual bands δ and numerical values for integration curves l_1, l_2, and l_3 corresponding to the bands a, b, and c in untreated polyamide fibers and fibers grafted with PAA dissolved in D_2SO_4 are shown in Table I. Apart from the values of chemical shifts shown in Table I, bands d over δ 9.0 ppm are also presented in Figure 1; they are interpreted as those derived from D_2SO_4. At δ 8.75 ppm another

band can also be observed, denoted with f in the mentioned figure, which can be accounted for by the hydrogen atom of the amide group. The signal at δ 0 ppm, denoted with e, corresponds to the TMS standard. To make the interpretation of the results easier, integration curves have also been included in the figures. The lowest absorption signals were used as reference points to minimize the error. The results from the integration curves denoted with l_1, l_2, and l_3, are that under band c (δ 1.9 ppm) there are three times more protons than under each of the remaining signals a and b. It is clear from the comparison of these values that $a : b : c = 1 : 1 : 3$. This means that if under bands a and b there are two protons each time, there must be six protons under band c. This is in agreement with the fragment of the PA6 chemical structure under consideration.

Figure 2 shows the spectral characteristics of PA6 fiber grafted with PAA. The positions of absorption bands of the grafted samples were not changed as compared with those for the basic spectrum (Fig. 1). However, the integration curves were altered and consequently the ratio $a : b : c$ was different, too. This means that some changes took place in the chemical structure of the grafted fibers in comparison with the untreated fibers. D_2SO_4 does not dissolve the PAA grafted fibers completely; and due to the "polyelectrolytic" effect in the fibers with high extent of grafting, the solutions show a high viscosity, which practically makes it impossible to take proper NMR spectra or can bring about an erroneous
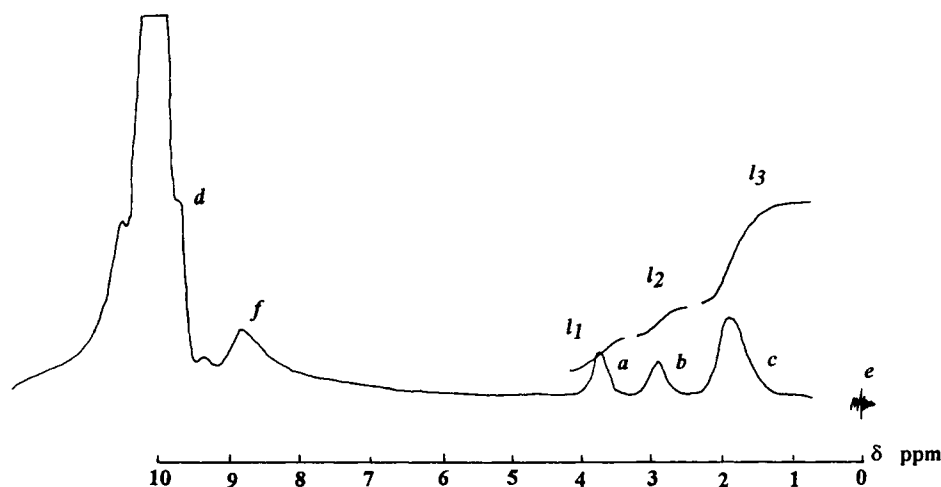
Figure 1   Spectral characteristics of untreated polyamide dissolved in D_2SO_4: a, absorption band from the group $-\overset{|}{N}-CH_2-$; b, absorption band from the group $-CH_2-\overset{|}{C}O$; c, absorption band from the group $-(CH_2)_3-$; d, absorption band from D_2SO_4; e, absorption band from TMS; f, absorption band from the group $-\overset{|}{N}-H$; l_1, integration curve for signal a; l_2, integration curve for signal b; l_3, integration curve for signal c.
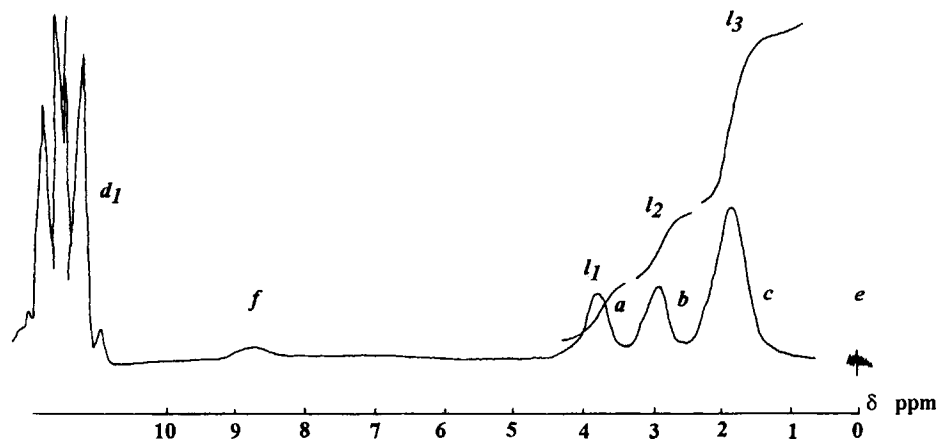
Figure 2 Spectral characteristics of polyamide fibers grafted with PAA with the extent of grafting $X = 0.24\%$ mol/g fiber dissolved in D_2SO_4; d_1, absorption band from the carboxylic groups of acrylic acid.

interpretation. Therefore, for more precise examination of the spectra of grafted fibers, formic acid was used as a solvent in the further section of the study. Nevertheless, it can be concluded from the spectra shown in Figure 2 that carbon in position α to the nitrogen of the amide group does not participate in the grafting process because there are no new absorption bands for methine groups. Moreover, using D_2SO_4 as a solvent, a broad absorption band was also observed in the NMR spectrum at δ 8.75 ppm (denoted with f in Figs. 1 and 2), which can be ascribed to the hydrogen atom at the nitrogen of the amide group. This band cannot be observed when using formic acid as a solvent because it is masked by the mentioned acid. Comparing this band in Figures 1 and 2 for untreated PA6 fibers with that for grafted fibers, it can be seen that it is most intensive for untreated samples and disappears almost completely for fibers with a high extent of grafting. This could suggest that the nitrogen—hydrogen bond of the amide group was replaced with a different arrangement of atoms. In the case when D_2SO_4 was

used as a solvent for grafted samples, absorption bands for carboxylic groups were observed, denoted in Figure 2 with d_1. They originated in acrylic acid, whose position of chemical shifts is outside the scale (offset). These bands are not observable when using formic acid as a solvent, because the absorption bands coming from the solvent in question are superimposed with the absorption bands of the carboxylic groups of PAA.

Interpretation of ^{1}H-NMR Spectra Recorded in Formic Acid

Figure 3 shows the spectral characteristics of untreated PA6 fibers dissolved in formic acid. Some differences occur as compared with the corresponding spectra recorded in D_2SO_4, namely formic acid as a strongly polar solvent changes the chemical shift of protons of substances dissolved in this acid.[43,44] When analyzing the spectral characteristics for the initial polyamide fiber (Fig. 3), it was found that the broad signal in the NMR spectrum at δ 3.0 ppm,

Table I Numerical Values of Chemical Shifts (δ) and for Integration Curves l_1, l_2, and l_3 Corresponding to Bonds a, b, and c

Sample	a		b		c	
	δ (ppm)	l_1	δ (ppm)	l_2	δ (ppm)	l_3
Untreated fibers	3.8	20	2.9	19	1.9	59
Fibers grafted with PAA, $X = 0.24\%$ mol/g	3.0	29	2.1	30	1.2	90

Fibers are polyamide fibers untreated and fibers grafted with PAA dissolved in H_2SO_4.
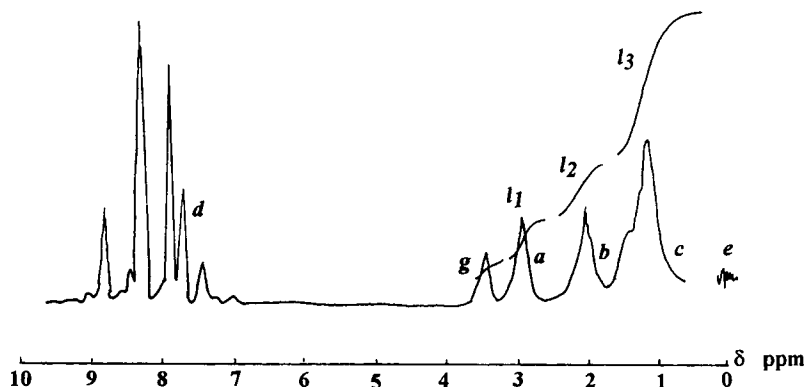
Figure 3 Spectral characteristics of untreated polyamide fibers dissolved in formic acid; a-c, l_1-l_3, as in Figure 1.

denoted with a, represents methylene groups at the nitrogen atom. The absorption band at δ 2.1 ppm, denoted with b in Figure 3, corresponds to the methylene groups adjacent to the carbonyl group; the signal in the considered NMR spectrum at δ 1.2 ppm, denoted with c in Figure 3, represents methylene groups near the methylene groups. In D_2SO_4 these groups brought about the absorption at a little different value of chemical shifts (Table I). The sharp singlet at δ 3.4 ppm, denoted with g in the Figure 3, should be treated as the band belonging to the hydroxyl group of formic acid, because this signal is not observable in the spectra recorded in D_2SO_4, and moreover, it appears at the same value of δ in the spectral characteristics of formic acid. The latter should be considered as a "blank test" carried out to make sure that the solvent shows no absorption bands at the same values of chemical shifts as the investigated PA6 samples. The absorption band located within the range of chemical shifts from 7 to 10 ppm, denoted with d in Figure 3, belongs to the solvent and will not be taken into account. The band at δ 0 ppm corresponds to the TMS standard and is denoted with e in all the figures. The values for integration curves, denoted as l_1, l_2, and l_3, presenting

the areas under bands a, b, and c, are shown in Table II. Analyzing the numerical values for integration curves shown in Table II, it was found that there are three times more protons under the c group than under each of the remaining bands. Thus, the same conclusion was reached as in the case with D_2SO_4 being used.

Interpretation of NMR Spectra of Thermally Oxidized PA6 Fibers Recorded in Formic Acid

From the spectral characteristics of PA6 fibers oxidized at an elevated temperature (393 K) in air for 10, 20, and 30 min, no fundamental changes in chemical shifts of the oxidized PA6 fibers occurred in comparison with the untreated fibers. Therefore, there are no spectral NMR characteristics in the subsequent figures of the investigated samples. The numerical values for integration curves l_1, l_2, and l_3 corresponding to the bands a, b, and c, and mutual relations of particular groups for oxidized PA6 fibers are shown in Table II.

The absence of new absorption signals observed for methine groups at δ 4.8–6.1 ppm and at δ 3.4–3.7 ppm[40,41] may suggest that the hydroperoxide

Table II Numerical Values of Integration Curves and Mutual Ratios of Particular Groups in Polyamide Fibers Oxidized at 393 K

Sample	Oxidation Time (min)	Values for Integration Curves			Mutual Ratios of Particular Groups		
		l_1	l_2	l_3	a	b	c
Untreated	0.0	29.0	30.0	90.0	1.00	1.00	3.00
1	10.0	25.0	22.0	66.0	1.14	1.00	3.00
2	20.0	22.0	18.5	55.0	1.19	1.00	3.00
3	30.0	32.0	26.0	78.0	1.23	1.00	3.00

groups resulting from the oxidation of PA6 fibers are absent at the mentioned methine groups, but are present at the nitrogen atom of the amide group. This is confirmed by the broadened band at δ 3.0 ppm that is characteristic of methylene groups a at the nitrogen atom. Thus, it can be concluded that the oxygen of hydroperoxide groups in oxidized PA6 fibers is added to the nitrogen atom of the amide group, and the absorption signal of the new bonds is under the outline of the absorption band characteristic of group a at the chemical shift value δ 3.0 ppm. It follows from the values for integration curves given in Table II for the samples oxidized for 10, 20, and 30 min, that the value of group a, defined by l_1 in relation to group b increases, which testifies to the addition of new groups to the nitrogen atom.

From Table II it can also be seen that if the hydroperoxide groups resulting from polyamide oxidation were formed at the carbon atom in position α to the amide group, then it should be expected that beside absorption bands a, b, and c, new signals would appear in the NMR spectrum of the oxidized samples corresponding to the methine group adjacent to the methylene group and to the methine group adjacent to the nitrogen with the appropriate values of chemical shifts. So, it is most likely that the initiation of PA6 fibers with the atmospheric oxygen at an elevated temperature results in the formation of active centers at nitrogen atoms of the amide groups.

Interpretation of NMR Spectra of PA6 Fibers Grafted with PAA Recorded in Formic Acid

The spectral NMR characteristics of PA6 fibers grafted with PAA with various extents of grafting (from 0.071 to 0.51% mol/g fiber) are similar and show no changes in the values of chemical shifts. Only the areas under the outlines of the appropriate NMR spectra, corresponding to integration curves, were changed. That is why no spectra of these samples are given in this article. Table III contains only the numerical values of l_1, l_2, and l_3 corresponding to the absorption bands of groups a, b, and c for grafted fibers with various extents of grafting.

The thermal oxidation of PA6 fibers and their grafting with PAA result in the formation of new chemical bonds that can be schematically shown as follows:

$$
\text{(A)} \quad -\underset{\underset{O}{\|}}{C}-\left[-\overset{\underset{|}{a\longrightarrow}}{N}-CH_2-\overset{c\longrightarrow}{CH_2}-CH_2-CH_2-\overset{b\longrightarrow}{CH_2}-\underset{\underset{O}{\|}}{C}-\right]_n-\overset{H}{\underset{|}{N}}-CH_2-
$$
$$
\underset{\underset{COOH}{|}}{O-(-CH_2-(CH)_m-)}
$$
$$
\overset{a'\longrightarrow}{}:b'
$$
$$(8)$$

or

$$
\text{(B)} \quad -\underset{\underset{O}{\|}}{C}-[-\overset{H}{\underset{H}{N}}-CH-CH_2-CH_2-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-]_n-\overset{H}{\underset{|}{N}}-CH_2-
$$
$$
\underset{\underset{COOH}{|}}{O-(-CH_2-CH)_m-}
$$
$$(9)$$

where $a = a'$, n is polymerization degree of PA6, and m is polymerization degree of PAA.

There is also a possibility that both structures A and B will appear simultaneously in the modified polyamide.

The absorption of carboxyl groups of PAA b' overlaps the absorption of the groups b of the polyamide ($b = b'$), while the absorption of methylene groups adjacent to oxygen overlaps that of methylene groups adjacent to nitrogen ($a = a'$) because these absorptions take place at the same values of the chemical shifts.

Based on the possible structures of the polyamide grafted with PAA (A and B in the above structure), one should expect a new narrow band of the group $-CH_2-O-$ of PAA denoted with a' in structure A, beside the band δ 3.0 ppm corresponding to bonds a, but it was not observed. There is only signal broadening at this value of the chemical shift and full band coverage ($-CH_2-O-$), which is also confirmed by the relation of the integration curves.

From Table III the ratio $a : b : c$ in the grafted fibers is 1 : 1 : 2.93 which just corresponds to the extent of grafting X = 0.071% mol/g fiber. For grafted PA6 fibers with the extent of grafting X = 0.51% mol/g fiber, it can be seen that the ratio of particular values of integration curves corresponding to groups a, b, and c is 1 : 1 : 2.41. The increase in the grafting extent of PAA on the polyamide is accompanied by changes in the ratio $a : b : c$. Namely, the intensity of band a corresponding to the methylene groups adjacent to nitrogen and oxygen

$$
\begin{matrix} -N-CH_2- \\ | \\ O-CH_2- \end{matrix}
$$

and the intensity of band b corresponding to the methylene groups in the surroundings of carbonyl groups $-CH_2-CO-$ increase, while the intensity of band c corresponding to the methylene groups in the surroundings of methylene groups $-(CH_2)_3-$ decreases. This is consistent with the theoretical calculations. This can also be clearly seen in Figure 4 that shows the dependence of absorption band c in relation to a and b on the extent of grafting polyamide fibers with PAA. This dependence can be given by the linear equation:

Table III   Numerical Values of Integration Curves and Mutual Ratios of Particular Groups in Polyamide Fibers with Various Extents of PAA Grafting

Sample No.	Extend of Grafting with PAA % mol/g	Wt %	Values of Integration Curves l_1	l_2	l_3	Ratios of Particular Groups a	b	c
0	Untreated		29.0	30.0	90.0	1	1	3.00
1	0.071	5.15	29.0	30.0	88.0	1	1	2.93
2	0.079	5.70	30.0	30.0	87.0	1	1	2.90
3	0.110	7.79	26.0	26.0	74.5	1	1	2.87
4	0.150	10.52	22.0	22.0	62.0	1	1	2.82
5	0.180	13.10	22.0	23.0	64.5	1	1	2.80
6	0.210	15.00	35.0	36.0	99.5	1	1	2.76
7	0.240	17.05	26.5	27.0	73.5	1	1	2.72
8	0.320	22.94	20.0	20.0	53.0	1	1	2.65
9	0.370	26.47	22.0	23.0	59.5	1	1	2.59
10	0.430	30.65	20.0	21.0	53.0	1	1	2.52
11	0.510	37.06	28.0	29.0	70.0	1	1	2.41

$$Y = -0.016X + 3 \qquad (10)$$

where X is extent of grafting polyamide fibers with PAA (wt %) and Y is absorption intensity of c in relation to a and b.

From Figure 4 the ratio $a : b : c$ can be anticipated for higher extents of grafting polyamide fibers with PAA. For example, for fibers with 50 wt % grafting, it can be expected that $a : b : c = 1 : 1 : 2.25$; for
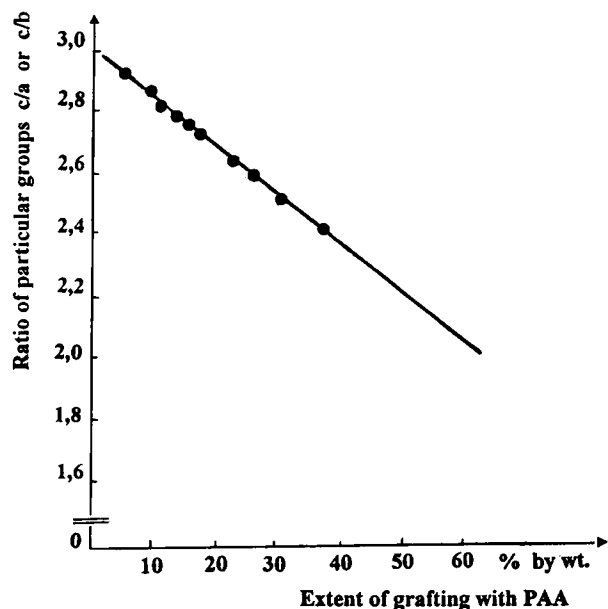

Figure 4   Relationship characterizing the absorption intensity of group c in relation to a and b.
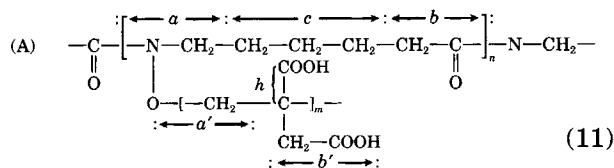
fibers with 100 wt % grafting this ratio is likely to be $1 : 1 : 1.5$. This is consistent with theoretical calculations.

Considering the spectra of polyamide fibers grafted with PAA, recorded in formic acid as a solvent, it can be suggested that the grafting process does not take place at the carbon in position α to the nitrogen of the amide bond, because beside the signals appearing in these spectra, new absorption bands of the methine groups in the appropriate surroundings should be observable. So, in the NMR spectrum beside the absorption band of groups a, b, and c, the appearance of a new distinct signal of the methine group should be expected adjacent to the methylene group at δ 3.4–3.7 ppm and an absorption band of the group —CH—N— at δ 4.8–6.1 ppm. Because none of them have been observed, it can be concluded with a high probability that the grafting does not take place at the carbon atom in position α to the amide group.

Interpretation of NMR Spectra of PA6 Fibers Grafted with PIA Dissolved in Formic Acid

Thermal oxidation of PA6 fibers and their subsequent grafting with PIA can result, in accordance with the previous suggestion, in copolymers with structures in which the addition of the vinyl polymer takes place at the nitrogen atom of the amide group according to structure A or the carbon atom in position α to the amide group (structure B), with the

appearance of both structures at the same time also being possible.

(A) $-\text{C}\!\!\begin{bmatrix}-\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}-\end{bmatrix}_n\!\!-\text{N}-\text{CH}_2-$ (11)

or

(B) $-\text{C}\!\!\begin{bmatrix}-\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}-\end{bmatrix}_n\!\!-\text{N}-\text{CH}_2-$ (12)
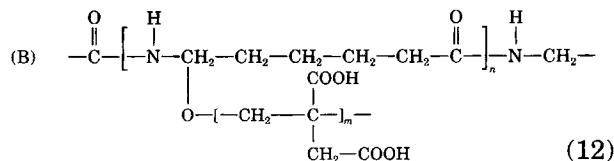
where $a = a'$, n is as previously, and m is polymerization degree of PIA.

NMR spectra were taken for the samples of grafted PA6 fibers with the extent of grafting X = 0.013, 0.022, and 0.026% mol/g. Analyzing the obtained spectra, it was found that there occur the same absorption bands for groups a, b, and c and at the same values of chemical shifts in comparison with the spectra of PA6 fibers grafted with PAA. Thus, in this article there are no figures of spectra of PA6 fibers grafted with PIA. Only the numerical values for integration curves are shown in Table IV.

The difference between the compared PIA and PAA spectra consists also of the fact that beside the aforementioned absorption bands at δ 1.2 and 3.0 ppm, there is a small signal at δ 2.5 ppm, denoted with h in the mentioned formula (11), that can be ascribed to the group $-\text{C}-\text{COOH}$. According to the available data,[40] this group appears at δ 2.4–2.7 ppm. There is also an amplification of the signal of

$-\text{CH}_2-\text{CO}-$ b in relation to a $-\text{N}-\text{CH}_2$ read from the integration curves.

Table IV given below contains the numerical values for integration curves l_1, l_2, and l_3 for particular absorption bands of groups a, b, and c.

It follows from Table IV that the difference between the values of curves l_1 and l_2 for fibers with 1.75 wt % grafting of PIA (Table IV, item 1) is 3, while the appropriate differences for samples with grafting of 2.88 and 3.33 wt % are 4 and 7, respectively. The low grafting extents of polyamide fibers grafted with PIA do not enable a closer interpretation of these spectra. Nevertheless, it can be concluded that the addition of PIA takes place at the nitrogen atom of the amide group. This is confirmed, as in the case of PAA grafts, by the lack of new absorption bands for the methine group adjacent to the methylene group and for the methine group adjacent to the nitrogen atom of the amide group.

Interpretation of ¹H-NMR Spectra of PA6 Fibers Grafted with PVP Dissolved in Formic Acid

As a result of grafting PVP onto PA6 fibers, the formation of the following structures (A or B) or the appearance of both structures at the same time can be expected, similar to the PAA and PIA grafts:

(A) $-\text{C}\!\!\begin{bmatrix}-\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}-\end{bmatrix}_n\!\!-\text{N}-\text{CH}_2-$ (13)
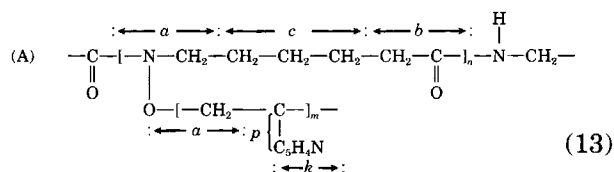
or

Table IV Numerical Values for Integration Curves and Mutual Ratios of Particular Groups in Polyamide Fibers Grafted with Various Extents of PIA Grafting

Sample No.	Extent of Grafting with PIA		Values for Integration Curves			Ratios of Particular Groups		
	% mol/g	Wt %	l_1	l_2	l_3	a	b	c
0	Untreated		29	30	90	1.0	1.00	3.0
1	0.013	1.75	21	24	64	1.0	1.14	3.0
2	0.022	2.88	20	24	60	1.0	1.20	3.0
3	0.026	3.33	31	31	90	1.0	1.22	3.0

Figure 5 Spectral characteristics of PA fibers grafted with PVP with the extent of grafting X = 0.038% mol/g dissolved in formic acid; k, absorption band from the group $-C_5-H_4-N$ and p, absorption band from the group $-CH-$ adjacent to $-C_5-H_4-N$. The remaining denotations are as in Figure 1.
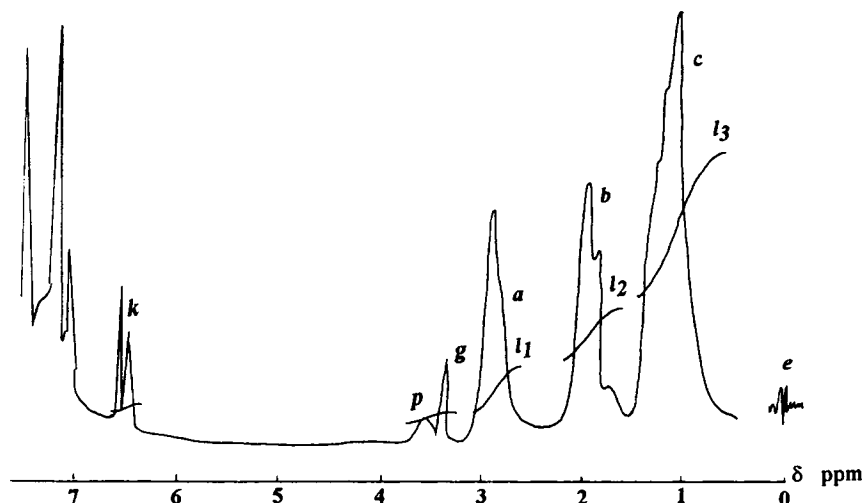
(B) $-CH_2-\overset{\overset{O}{\|}}{C}-[-\overset{\overset{H}{|}}{N}-CH-CH_2-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-]_n-\overset{\overset{H}{|}}{N}-$

$O-[-CH_2-CH]_m-$
$\quad\quad\quad\quad C_5H_4N$ (14)
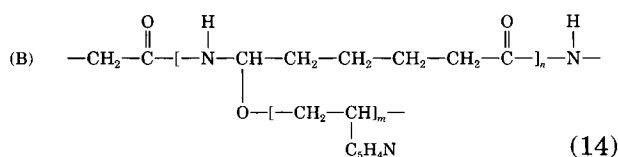
where $a = a'$, n is as previously, and m is polymerization degree of PVP.

NMR spectra were taken for the samples with the following extent of PVP grafting: 0.010, 0.023, and 0.038% mol/g fiber. In Figure 5, the NMR spectrum of the fiber containing 0.038% mol/g fiber is shown as an example. Table V contains the numerical values for integration curves l_1, l_2, and l_3 corresponding to the absorption bands of a, b, and c for fibers with various extents of PVP grafting.

It is seen from the data in Table V that the absorption band of groups b is decreased as compared with a. Thus, the difference between a and b for fibers with 1.07 wt % PVP is 2 (Table V, item 1),

while the appropriate differences for fibers with 2.46 wt % PVP and 3.95 wt % PVP are 4 and 6, respectively. This means that a new band a' is hidden under band a, while bands b and c remain unchanged in relation to the untreated fibers. It is consistent with theoretical considerations that the addition of PVP takes place according to structure A.

In Figure 5 that illustrates the spectral characteristics of PA6 fibers grafted with PVP, in addition to signals a, b, and c, illustrating particular protons with their surroundings, new absorption bands can be observed. Thus, a small signal at δ 3.6 ppm, denoted in Figure 5 and formula (13) with p, corresponds probably to the methine group adjacent to the pyridine group; the duplet at δ 6.6 ppm can testify to the appearance of the group $-C_5H_4N$, denoted with k. The low grafting extents of PA6 fibers grafted with PVP, as in the case of PIA grafts, do not enable a more detailed interpretation of these spectra. Nevertheless, it can be concluded from the obtained

Table V   Numerical Values for Integration Curves and Mutual Ratios of Particular Groups in Polyamide Fibers with Various Extents of PVP Grafting

Sample No.	Extent of Grafting with PVP		Values of Integration Curves			Ratios of Particular Groups		
	% mol/g	Wt %	l_1	l_2	l_3	a	b	c
0	Untreated		29	30	90	1.0	1.03	3.10
1	0.010	1.07	38	36	108	1.0	0.94	2.84
2	0.023	2.46	48	44	132	1.0	0.91	2.75
3	0.038	3.95	51	45	135	1.0	0.88	2.64

spectral characteristics for these polymers that the addition of PVP takes place at the nitrogen atom of the amide group. This is confirmed, as in PAA and PIA grafts, by the lack of absorption bands of the methine group that should be expected if the grafting were accomplished according to structure B.

CONCLUSION

Basing on the performed ^{1}H-NMR examination, it is highly probable that the active centers in PA6 fibers generated by the thermal–oxidative initiation process in air, are formed at the nitrogen atoms of the amide groups. This is confirmed by broadening of the absorption band of the methylene group a adjacent to the nitrogen atom.

Prolongation of the oxidation time from 10 to 30 min brings about an increase in the number of active centers. This is confirmed by the increase of the absorption band for group a, determined by integration curve l_1 in relation to the absorption band of group b, that in turn is determined by integration curve l_2.

Of the two solvents used in the study (D_2SO_4, HCOOH), formic acid turned out to be better for recording NMR spectra. Deuterated sulfuric acid did not dissolve the grafted samples to a sufficient extent.

Comparing bands f (which are ascribed to the hydrogen atom at the lactam nitrogen, being observable only when using D_2SO_4) of untreated fibers and PAA grafted fibers with growing grafting extent, one can notice that this band shows the highest intensity for untreated fibers and disappears completely in the case of grafted fibers with high grafting extent (Figs. 1, 2). This would suggest that the nitrogen — hydrogen bond of the amide group was replaced with another atom arrangement.

The spectral examination of polyamide fibers oxidized and grafted with PAA, PIA, and PVP using deuterated sulfuric acid and formic acid as solvents leads to the conclusion that the generation of active centers in polyamide fibers and the grafting of the mentioned polymers took place at the nitrogen atoms of the amide groups. This is shown by the broadening of the absorption band a of the methylene group adjacent to the nitrogen as well as by the lack of a new band of the methine groups, assuming that the grafting could take place at the carbon atom of the methylene group in position α to the amide group.

On this basis, it can be concluded with a high probability that the activation of fibers by heating in air and the subsequent grafting process take place according to the following:

$$-[-(CH_2)_5-CONH-]_n \xrightarrow[\text{heating}]{O_2} [-(CH_2)_5-\underset{|}{\underset{OOH}{CON}}-]_n$$

$$\xrightarrow{\text{decompostion}} -[-(CH_2)_5-\underset{|}{\underset{O^\circ}{CON}}-]_n + {}^\circ OH \xrightarrow{nM}$$

$$-[-(CH_2)_5-\underset{|}{\underset{O(X)_m}{CON}}-]_n- \quad (15)$$

where M is the vinyl monomer and X are chains of PAA, PIA, or PVP.

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