

Study of Radiation-Induced Graft Polymerization of Vinyl Monomers to Cellulose by Infrared Spectroscopy. I. Cellulose-Polyacrylonitrile Copolymers

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Synopsis

Infrared spectral analysis has been applied for the study of cotton-polyacrylonitrile copolymers prepared by using the preirradiation method. The degree of grafting was determined from the absorption at 2249 cm.^{-1} , which is characteristic of the polyacrylonitrile spectrum, with an accuracy of $\pm 1.5\%$.

INTRODUCTION

One of the methods of modifying the properties of cotton consists in the synthesis of grafted cotton copolymers and vinyl polymers, e.g., polyacrylonitrile (PAN). The introduction of only a small amount of nitrile groups into the structure of cotton markedly improves some of the physical, chemical, and mechanical properties, e.g., resistance to moisture and to microorganisms, abrasion resistance, etc.

Graft copolymerization of cotton and PAN can be initiated, for example, by the redox system of ceric ions,^{1,2} ozonization,³ or high-energy γ -radiation.³⁻⁵

In our laboratory we used the radiation method of initiation of grafting according to the modified preirradiation method described by Kobayashi⁷ for the preparation of a cotton-polyacrylonitrile copolymer. The radiation source was a Van de Graaff accelerator of 2 M.e.v. maximum energy.

The composition and the structure of the prepared copolymers were studied by a method of infrared spectral analysis, used previously by some authors.^{4,9,10}

EXPERIMENTAL

Preparation of Samples

The starting material for the preparation of copolymers was a piece of Callot cotton fabric of the following specifications: material: 40's cotton count, combed; set: 540/230; weight: 105 g./m.².

Samples approximately 3.5 g. in weight, prepared from the cotton fabric, were allowed to swell in 3% hydrogen peroxide and irradiated after swelling.

Irradiation of Samples

The samples were irradiated on a Van de Graaff electron accelerator to a dose of 1.5×10^6 rad, the dose rate being 5×10^6 rad/min. and the energy rate 1.5 M.e.v.

Grafting Technique

After irradiation, the cotton fabric samples were left another 30 min. in the peroxide solution, whereupon they were centrifuged and dried in air at room temperature.

The acrylonitrile used for further treatment of the samples was purified by redistillation at reduced pressure shortly before use.

The dry samples of irradiated cotton fabric were dipped into a mixture of acrylonitrile (AN), methyl alcohol, and water of varying composition depending on the required degree of grafting in test tubes 6 cm. in diameter and 20 cm. in length. The amount of AN in the mixtures was within the range 5–15 vol.-%, the amount of methyl alcohol in the range of 20–30 vol.-%. Nitrogen was bubbled through the individual mixtures and after removal of oxygen from the mixture and from the test tube, the samples were heated for 1 hr. in a water bath at 70°C. under reflux. As soon as the reaction took place, which was shown by the solution becoming turbid, the fabric samples were taken out, washed with distilled water, and hot-extracted with dimethylformamide for 6 hr., the homopolymer formed being thus removed. After extraction, the samples were dried at 110°C. and weighed.

The uniformity of grafting was followed by staining the grafted fabric with Astrazonblau B and the degree of grafting was, for the sake of comparison with the results of infrared analysis, rechecked by determining the nitrogen content in the copolymer by the Kjeldahl method.

Infrared Spectral Analysis

The potassium bromide pressed disk technique⁶ was used to study the behavior of the cotton-polyacrylonitrile copolymers in the infrared region.

Pieces of suitable size were prepared from the copolymer fibers by cutting on a hand microtome (100 μ measured microscopically). An 0.008-g. sample prepared in this way was mixed with 0.8 g. potassium bromide, dried at 110°C. and the mixture was homogenized by short grinding (2 min.) in a vibratory grinder, model Ardenne. The obtained homogeneous mixture was put in a vacuum pressing mold and after 5 min. evacuation pressed at a pressure of 18 tons/cm.². The transparent disk prepared in this way had a diameter of 2 cm. and was 1 mm. thick.

The infrared spectra were recorded on a Zeiss double-beam recording spectrometer model UR 10, in the spectral region 4000–400 cm.⁻¹. For

the 4000–1800 cm^{-1} region a lithium fluoride prism was used, for the 1800–700 cm^{-1} region a sodium chloride prism was used, and for the 700–400 cm^{-1} region a potassium bromide prism was used.

RESULTS

A number of copolymers of cotton and PAN of varying composition was prepared by using the preirradiation method.⁷ The PAN content in the individual copolymers was determined from the difference in the weight of the samples before and after grafting according to the relation:

$$\text{Degree of grafting} = [(V_r - V_o)/V_o] \times 100 \quad (1)$$

where V_r is the weight of grafted sample and V_o is the weight of original sample.

The composition and the structure of the prepared copolymers were studied by the method of infrared spectral analysis, using the KBr pressed disk technique.

The infrared spectra of the copolymers with varying PAN content, measured in the 4000–400 cm^{-1} region, were compared with the infrared spectrum of pure cotton. Figure 1 shows the spectrum of cotton (curve 1) and of its copolymer containing 42.9% PAN (curve 2).

It can be seen from Figure 1 that the absorption bands in the copolymer spectrum remain essentially unchanged; only in the bands corresponding to the hydroxyl groups ($\nu_{\text{OH}} = 3380 \text{ cm}^{-1}$, $\delta_{\text{C-OH}} = 1163 \text{ cm}^{-1}$) was a certain decrease in intensity observed; this was previously reported by some authors.^{8,10}

The effects of radiation on the cotton structure at a low radiation dose ($1.5 \times 10^6 \text{ rad}$) are negligible¹³ and do not produce remarkable changes in the infrared spectrum.

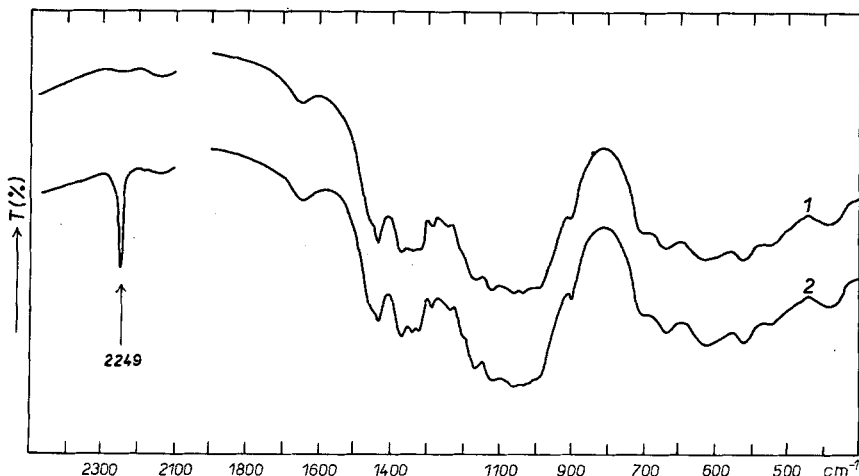


Fig. 1. Infrared spectra of (1) cotton and (2) cotton-PAN copolymer containing 42.9 wt.-% PAN.

The spectra of copolymers differ from the spectrum of pure cotton by an absorption band at 2249 cm^{-1} , which is characteristic for the PAN spectrum and corresponds to the valence vibration of the $-\text{C}\equiv\text{N}$ bond. Since the intensity of this band is dependent on the amount of PAN in the copolymer, the 2249 cm^{-1} band can be used for the quantitative evaluation of the composition of the prepared copolymer samples.

The absorption band at 2249 cm^{-1} was determined by the baseline method.¹¹

Absorbance of the band of definite wavenumber (ν) can be calculated by use of eq. (2).¹²

$$A(\nu) = \log [I_0(\nu)/I(\nu)] \\ = \sum_{i=1}^{i=n} k_i(\nu)c_i d + K(\nu, c_i, d) \quad (2)$$

where k_i is the absorbance coefficient of individual components of the sample, c_i is concentration, d is thickness of the sample, and K is a coefficient dependent on wavenumber, preparation, and thickness of the sample.

The coefficient K from eq. (2) can be eliminated by using the baseline methods, and thus the possible differences in the thickness of measured and reference samples and in the magnitude of the loss of light.

For the calculation of the absorbance at $\nu_2 = 2249 \text{ cm}^{-1}$ two points at wavenumbers $\nu_1 = 2210 \text{ cm}^{-1}$ and $\nu_3 = 2290 \text{ cm}^{-1}$ equidistant from the equidistant from the absorption peak point ν_2 were chosen and the baseline was drawn. In this case the absorbance coefficients $k_1(\nu_1)$ and $k_1(\nu_3)$ are equal and the simple equation would then be:

$$A_{(\nu)} = \log [I_b(\nu_2)/I(\nu_2)] \\ = k_1(\nu_2) - k_1(\nu_3) cd \quad (3)$$

where I_b is the intensity of the band ν_2 measured from the baseline.

The calibration curve was obtained from spectra of the mixtures of potassium bromide and PAN containing between 0.2–3.2 mg. PAN. In calculating the weight percentage of PAN in the individual mixtures ac-

TABLE I
Absorbance at the 2249 cm^{-1} Band in Spectra of KBr-PAN Mixtures

Sample	PAN, mg.	PAN, wt.-%	A_{2249}
1	0.2	2.6	0.015
2	0.4	5.3	0.031
3	1.2	17.6	0.116
4	1.6	25.0	0.163
5	2.0	33.3	0.218
6	2.4	42.9	0.275
7	3.2	66.7	0.430

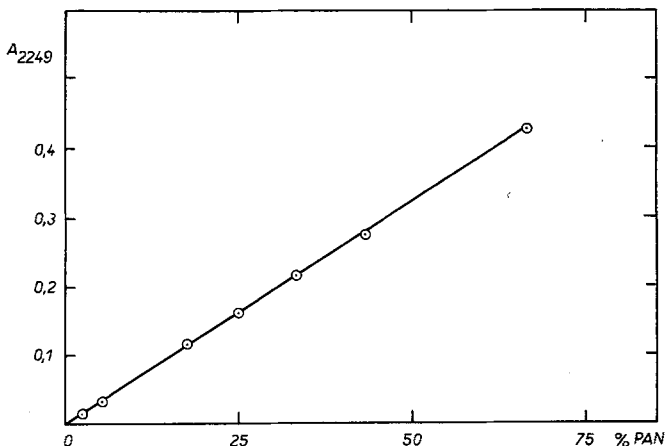


Fig. 2. Calibration curve for PAN content in the copolymer.

According to eq. (1), the weight of PAN was related to the total weight of the copolymer sample in the disks, i.e., $V_r = 8$ mg.

The disks prepared from the mentioned mixtures were measured in the 2100–2350 cm^{-1} region and from the obtained spectra the absorption band at 2249 cm^{-1} was evaluated by the baseline method described above. The absorbance values of this band obtained by averaging three individual measurements are presented in Table I and the dependence of A_{2249} on the concentration of PAN is plotted in Figure 2. The obtained calibration curve was used to evaluate the spectra of the prepared copolymers.

The percentage content of PAN in the individual copolymers, estimated by the method of infrared spectra analysis, is shown in Table II and compared with the values obtained from the weight of the samples before and after grafting by calculation according to eq. (1). The individual values represent again the average of three measurements.

It can be seen from Table II that the maximum difference between the value estimated by infrared spectroscopy and the value obtained by weighing amounts to $\pm 2.5\%$. Similar results were also obtained on comparing

TABLE II
Absorbance of the 2249 cm^{-1} Band in the Spectra of Copolymers

Sample	A_{2249}	PAN, % (calc. from IR)	PAN, wt.-%	Difference, %
1	0.062	9.7	10.3	-0.5
2	0.119	18.5	18.2	+0.3
3	0.187	29.0	28.3	+0.7
4	0.225	34.5	36.3	-1.8
5	0.297	45.8	46.6	-0.8
6	0.309	47.5	50.0	-2.5

the results of infrared spectral analysis and of the method based on nitrogen estimation.

DISCUSSION

Infrared spectroscopy has been used to investigate the radiation grafting of vinyl monomers on cotton and to determine the structural and analytical composition of the copolymers formed.

Analysis of the infrared spectra of cotton-polyacrylonitrile copolymers shows that at high-energy irradiation there is no acrylonitrile homopolymerization on the cotton fibers but an actual grafting process, as was already stated by some authors.^{10,3}

Proof of this is the reduced intensity of the absorption bands of hydroxyl groups and an intense band at 2249 cm^{-1} , which is assigned to the valency vibration of the nitrile group. The intensity of this band upon elimination of the homopolymer, is not affected by further extraction with dimethylformamide.

By the method of infrared spectral analysis has proved useful because of its accuracy, speed, and the fact that only a small sample is required. The individual samples were estimated with an accuracy of $\pm 1.5\%$, but for the samples with a PAN content exceeding 50% the error was higher. This can be explained by the fact that fibers with a higher PAN content exhibit a reduced strength and when cut on the microtome, particles of sufficiently small size cannot be prepared. Through scattering and reflection of light on the bigger particles, less light is transmitted. Since fibers with such a high PAN content are of no importance for practical use, infrared spectral analysis remains one of the most suitable methods for the study of the composition of copolymers.

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Résumé

L'analyse spectrale infrarouge a été appliquée à l'étude de copolymères de coton-polyacrylonitrile préparés en utilisant la méthode par préirradiation. Le taux de greffage était déterminé par absorption à 2249 cm^{-1} , bande caractéristique du spectre polyacrylonitrile avec une précision d'environ 1.5%.

Zusammenfassung

Die mit der Vorbestrahlungsmethode hergestellten Baumwolle-Polyacrylnitrilcopolymeren wurden infrarotspektroskopisch untersucht. Der Aufpfropfungsgrad wurde aus der für das Polyacrylnitrilspektrum charakteristischen Absorptionsbande bei 2249 cm^{-1} mit einer Genauigkeit von $\pm 1,5\%$ bestimmt.

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