

## **Study of Radiation-Induced Graft Polymerization of Vinyl Monomers to Cellulose by Infrared Spectroscopy. II. Cellulose-Polystyrene Copolymers**

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### **Synopsis**

Infrared spectral analysis has been applied for the study of cotton-polystyrene copolymers prepared by using the preirradiation method. The degree of grafting was determined from the absorption at  $700\text{ cm}^{-1}$ , which is characteristic of the polystyrene spectrum, with an accuracy of  $\pm 1.5\%$ .

### **INTRODUCTION**

Some of the physical, chemical, and mechanical properties of cotton can be modified by formation of grafted cotton copolymers and vinyl polymers. The preparation of radiation-induced cotton-polyacrylonitrile graft copolymers was described in a previous publication.<sup>1</sup> A similar procedure has been applied in our laboratory for preparing cotton-polystyrene copolymers.

The composition and the structure of the prepared copolymers were studied by a method of infrared spectral analysis.

### **EXPERIMENTAL**

#### **Preparation of Samples**

A piece of Callot cotton fabric, described in the previous paper,<sup>1</sup> was used for the preparation of copolymers. Samples prepared from the cotton fabric, having a weight of about 3.5 g, were irradiated after swelling in 3% hydrogen peroxide.

#### **Irradiation of Samples**

The samples were irradiated on a Van de Graaff electron accelerator to a dose of  $1.5 \times 10^6$  rad at a dose rate of  $5 \times 10^6$  rad/min and an energy rate of 1.5 MeV.

### Grafting Technique

After irradiation, the cotton fabric samples were left for 30 min in the peroxide solution and then centrifuged and finally dried in air at room temperature.

Styrene (produced by Kaučuk, N.C., Kralupy n/V.) used for further treatment of the samples was purified by redistillation<sup>1</sup> under reduced pressure shortly before use.

The grafting technique was identical to that reported previously.<sup>1</sup>

The uniformity of grafting was followed by staining the grafted fabric with Ostacetate Blue T2R and by examining the fabric under ultraviolet light on a Fluotest instrument (Original Hanau, Germany).

### Infrared Spectral Analysis

The samples of cotton and polystyrene copolymers for examination in the infrared region were prepared by cutting on a hand microtome and by the potassium bromide pressed-disk technique.<sup>1</sup>

The infrared spectra were recorded on a Zeiss double-beam recording spectrophotometer model UR 10, in the spectral region 4000–400  $\text{cm}^{-1}$ .

## RESULTS

A series of cotton–polystyrene copolymers of various compositions were prepared by using the preirradiation method.<sup>2</sup> The content of the grafted polystyrene was determined according to the relation:

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

where  $V_r$  is the weight of the grafted sample and  $V_v$  is the weight of the original sample.

The structure and the quantitative composition of the copolymers were studied by the method of infrared spectral analysis. The infrared spectrum of the cotton starting material (Fig. 1, curve 1) was compared with the spectrum of the cotton–polystyrene copolymer containing 33.3% polystyrene (Fig. 1, curve 2).

Quantitative determination of the polystyrene content in copolymer by infrared spectral analysis is substantially more difficult than the determination of the polyacrylonitrile content. The characteristic absorption bands of polystyrene appear in most cases in the same spectral regions as the bands of cotton, as shown in Figure 1. The absorption bands of polystyrene in the infrared region 3200–70  $\text{cm}^{-1}$  were analyzed by Ling and Krimm.<sup>3</sup> For the calculation of the degree of grafting, the most suitable appears to be the medium strong absorption band at 700  $\text{cm}^{-1}$  which can be observed in a spectral region where no intense characteristic bands appear in the spectrum of cotton.

When calculating the degree of grafting from the intensities of other absorption bands characteristic for polystyrene, e.g., the band at 1602  $\text{cm}^{-1}$  ( $\nu_{\text{C}=\text{C}}$  of benzene ring) or at 3030  $\text{cm}^{-1}$  (asym.  $\nu_{\text{CH}_2}$ ), no exactly linear

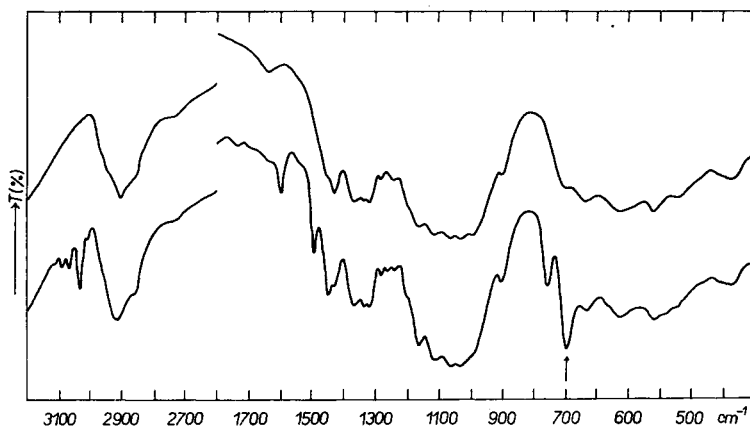


Fig. 1. Infrared spectra of (1) cotton and (2) cotton-polystyrene copolymer containing 33.3 wt-% polystyrene.

dependence was found. The absorption band at  $700\text{ cm}^{-1}$  represents the deformation vibration of the  $-\text{CH}-$  group of the monosubstituted benzene ring ( $\delta_{\text{CH}} = 700\text{ cm}^{-1}$ ), and it has been found that the intensity of this band is dependent on the amount of polystyrene in the copolymer.

The analyzed absorption band at  $700\text{ cm}^{-1}$  was evaluated by the method of absorbance differences<sup>4</sup> based on measuring the absorbencies of two not too widely separated wavenumbers.

Absorbance of the band of definite wave number ( $\nu$ ) can be calculated by use of eq. (2):<sup>5</sup>

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

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 wave number, preparation, and thickness of the sample.

Assuming that the term  $K$  of eq. (2) is independent of wave number, the difference of absorbencies  $Q(\nu_1, \nu_2)$  is given by the relation:

$$\begin{aligned} Q(\nu_1, \nu_2) &= A(\nu_1) - A(\nu_2) \\ &= \log [I_0(\nu_1)/I(\nu_1)] - \log [I_0(\nu_2)/I(\nu_2)] \\ &= \sum_{i=1}^{i=n} [k_i(\nu_1) - k_i(\nu_2)]c_i d \end{aligned} \quad (3)$$

This equation may be used in a rearranged form:

$$\log [I(\nu_2)/I(\nu_1)] = \sum_{i=1}^{i=n} [k_i(\nu_1) - k_i(\nu_2)] c_i d + \log [I_0(\nu_2)/I_0(\nu_1)] \quad (4)$$

For the double-beam instruments, the logarithm of the ratio of intensities in eq. (4) is as follows:

$$\log [I_0(\nu_2)/I_0(\nu_1)] = 0$$

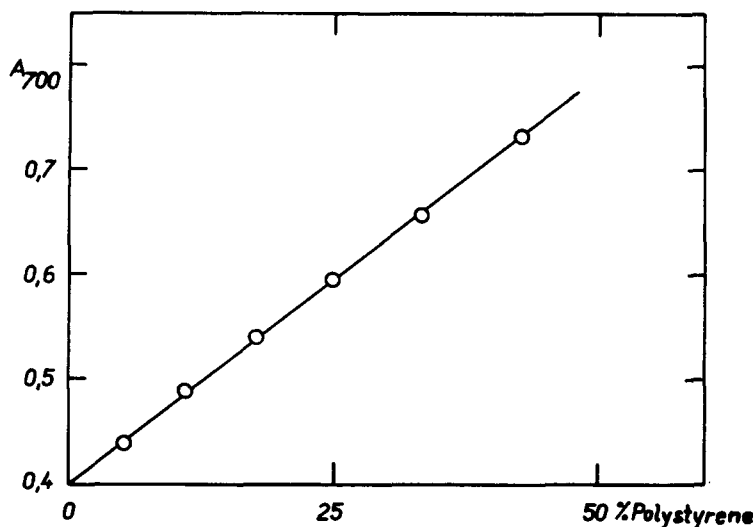


Fig. 2. Calibration curve for polystyrene content in the copolymer.

In evaluating the intensity of the band at  $700\text{ cm}^{-1}$ , the difference of absorbencies for the wave numbers  $\nu_1 = 700\text{ cm}^{-1}$  and  $\nu_2 = 810\text{ cm}^{-1}$  was calculated. In the region of wave number  $810\text{ cm}^{-1}$ , no absorption band was found in the copolymer spectrum (Fig. 1).

The calibration curve was obtained from spectra of the mixtures of potassium bromide and polystyrene containing 0.4–2.4 mg polystyrene.

In calculating the weight percentage of polystyrene in the individual mixtures according to eq. (1), the weight of polystyrene was related to the total weight of the copolymer sample in the disks, i.e.  $V_r = 8\text{ mg}$ .

The absorbance values of the analyzed band at  $700\text{ cm}^{-1}$  obtained by averaging three individual measurements are listed in Table I, and the dependence of  $A_{700}$  on the concentration of polystyrene is illustrated in Figure 2. The obtained calibration curve was used for evaluating the spectra of the prepared copolymers.

TABLE I  
Absorbance at  $700\text{ cm}^{-1}$  in Spectra of KBr–Polystyrene Mixtures

Sample	Polystyrene, mg	Polystyrene, wt-%	$A_{700}$
1	0.4	5.3	0.439
2	0.8	11.1	0.490
3	1.2	17.6	0.540
4	1.6	25.0	0.595
5	2.0	33.3	0.656
6	2.4	42.9	0.733

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

TABLE II  
Absorbance at 700  $\text{cm}^{-1}$  in the Spectra of Copolymers

Sample	$A_{700}$	Polystyrene, % (calcd from IR)	Polystyrene, wt-%	Difference, %
1	0.480	10.2	10.5	-0.3
2	0.533	16.7	16.3	+0.4
3	0.567	21.1	20.2	+0.9
4	0.692	37.7	38.5	-0.8
5	0.838	56.8	57.9	-1.1
6	0.952	72.2	75.9	-3.7

As may be seen from Table II, the maximum difference between the value estimated by infrared spectroscopy and the value obtained by weighing amounts to  $\pm 3.7\%$ . This high difference was however found only in case of samples containing more than 60% of grafted polystyrene.

## DISCUSSION

The method of infrared spectral analysis has proved to be a suitable method for the study of the radiation grafting of vinyl monomers. By evaluation of the infrared spectra of the prepared cotton-polystyrene copolymers their structure and analytical composition may be determined.

Of importance is the finding that the characteristic absorption bands of cotton are observable in the copolymer too, there being a certain decrease in intensity during the grafting process only in the bands corresponding to the valence vibration of the hydroxyl groups. At low doses ( $1.5 \times 10^6$  rad) no remarkable changes occur in the structure of cotton. The intensity of the absorption band at 700  $\text{cm}^{-1}$  upon elimination of the homopolymer is not affected by further extractions, which is the main proof of copolymerization.

The advantages of the method of infrared spectral analysis for the study of copolymers were already described.<sup>1</sup>

## References

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