

Gamma Radiation-Induced Graft Copolymerization of Divinylbenzene onto Cellulose Fabric

S. TRBOJEVIĆ-GOBAC,* M. VLATKOVIĆ, and Z. MEIĆ, *Rudjer Bošković Institute, P.O.B. 1016, 41001 Zagreb, Yugoslavia*

Synopsis

The extent of DVB grafting onto cellulose fabric increases with total gamma radiation dose up to 10–15 kGy while it decreases with the radiation dose rate. A quantitative analysis of DVB grafting has been attempted by means of IR spectroscopy using the baseline method. Characteristic bands were selected in the spectra of copolymers, namely, the cellulose band at 1160 cm^{-1} and DVB band at 798 cm^{-1} . The former band decreased and the latter increased with the degree of copolymerization, and the values were in accordance with the calibration straight line. An attempt to graft DVB onto cotton fabric previously grafted with styrene showed greater extent of copolymerization than with pure fabric.

INTRODUCTION

Methods of vinyl polymer grafting onto cellulose and modified textile properties of grafted fabrics have been the subject of numerous studies and their results have been reported in several review articles.^{1–4} Copolymers of cellulose and vinyl monomers are formed primarily through the free-radical mechanism, which can be easily induced by high-energy irradiation. The grafting of monofunctional vinyl compounds has been investigated quite extensively. With the exception of a few papers,^{5,6} however, there does not seem to be much information available on the grafting of the difunctional vinyl derivative of benzene, divinylbenzene (DVB), onto cellulose, which is expected to modify cellulose properties.

The purpose of the present study was to investigate the extent of the grafting process of DVB onto cotton cellulose by using gamma irradiation in order to induce copolymerization. The reactants were irradiated simultaneously at various dose rates and various total irradiation doses. Attempts were made to characterize the copolymers by IR spectroscopy.

The well-known crosslinking reaction of styrene with DVB⁷ led us to believe that this copolymer might be used indirectly for the modification of cellulose fabric properties. We examined therefore the radiation-induced DVB grafting onto cotton fabric previously grafted with styrene.

* Present address: Faculty of Economics, University of Zagreb, 41000 Zagreb, Yugoslavia.

EXPERIMENTAL

Materials

Unfinished cotton poplin was pretreated as is common with cotton fabrics; it was enzymatically desized and scoured, washed by boiling, peroxide bleached, and mercerized. In order to achieve uniform and thorough penetration of the monomer into the fabric, the pretreatment was completed by ethanol extraction in a Soxhlet apparatus and by boiling in an alkaline solution.

Divinylbenzene (Merck, 50% ethylvinylbenzene) was distilled at 316–317 K under a reduced pressure. Styrene (technical grade, from OKI Zagreb) was purified by double distillation under vacuum. Other chemicals were of reagent-grade purity.

Irradiation-Induced Grafting of DVB onto Cellulose Fabric

The simultaneous irradiation method involves the irradiation of cellulose substrate in a solution of monomer. Copolymerization is usually accompanied by the formation of a certain amount of homopolymer. The tentative investigations into the dependence of the extent of DVB grafting on the monomer concentration in the solution showed that the optimum composition of the monomer solution was DVB:methanol = 1:1. The weight ratio of DVB solution to cotton fabric was 10:1. The pretreated fabric was completely immersed in the solution and left to swell for 12 hr prior to gamma irradiation. Irradiations were done on a 1.1 PBq ^{60}Co source in the presence of air, at various total doses and dose rates.

Extraction of DVB Homopolymer and Yield Determination of Grafted DVB

The amounts of homopolymer and grafted DVB on the fabric were determined on previously weighed, dry samples of fabric of about 1 g (w_1). Reference samples for the determination of homopolymer contents were soaked in tetraline and dried at 378–383 K to constant weight (w_2). The grafted samples were then extracted with tetraline⁸ in a Soxhlet apparatus for 24 hr under reduced pressure. After extraction the samples were dried to constant weight (w_3). The DVB content in nonextracted samples was calculated as $[(w_2 - w_1)/w_1] \times 100$, and the percentage of DVB grafting was determined by the expression $[(w_3 - w_1)/w_1] \times 100$.

Grafting of DVB and Styrene to Cotton Fabric

DVB was grafted to cotton fabric samples which had been previously grafted with styrene as described before.⁹ The weight ratio of the grafting solution to the fabric was 10:1. The extraction of homopolymer and the determination of the graft extent were performed as described above.

Infrared Spectra

IR spectroscopy was used in our study to confirm the extent of DVB grafting to cellulose and to investigate some of the structural features, e.g., crosslinking. The KBr disc technique was used because the samples were insoluble in the usual solvents and the structure of the solid had to be preserved.

Samples were prepared by cutting the grafted fabric or other polymeric material taken for comparison into small pieces which were mixed with KBr powder and ground in a vibration mill. The best concentration was 3 mg sample and 100 mg KBr. The spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer.

RESULTS

The results of DVB grafting onto cotton cellulose fabric obtained by simultaneous irradiation are presented in Figures 1 and 2. The yield of pure DVB graft (Fig. 1) and the yield of DVB homopolymer graft in nonextracted samples (Fig. 2) are shown as a function of the total irradiation dose up to 10–15 kGy and of the radiation dose rate. Each point represents the mean of two measurements.

Table I gives the results of DVB grafting onto cotton fabric samples previously grafted with styrene. The radiation doses for the first grafting (styrene) are given in the second column, and for the DVB grafting, in the fourth column.

In the analysis of infrared spectra of any complex compound or mixture, it is important to properly select the most characteristic or "key" bands^{10,11} arising from group vibrations. The spectrum of the mechanical mixture of cellulose

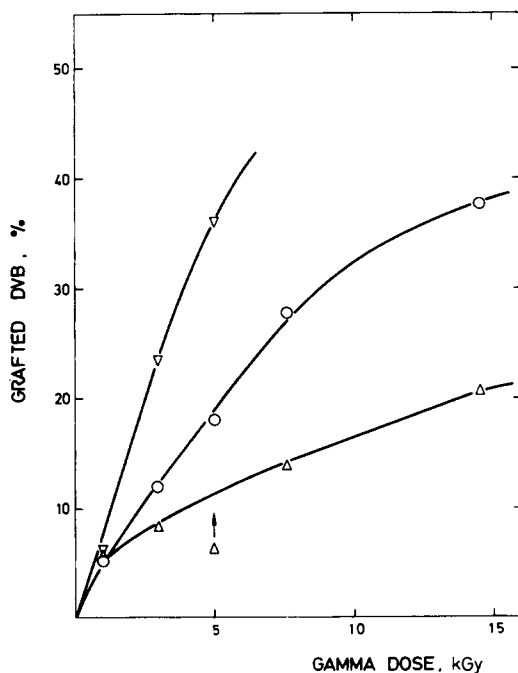


Fig. 1. Variation of extent of DVB grafting onto cotton fabric with increasing irradiation dose and irradiation dose rate: (▽) 10 mGy/sec; (○) 0.27 Gy/sec; (△) 1.73 Gy/sec.

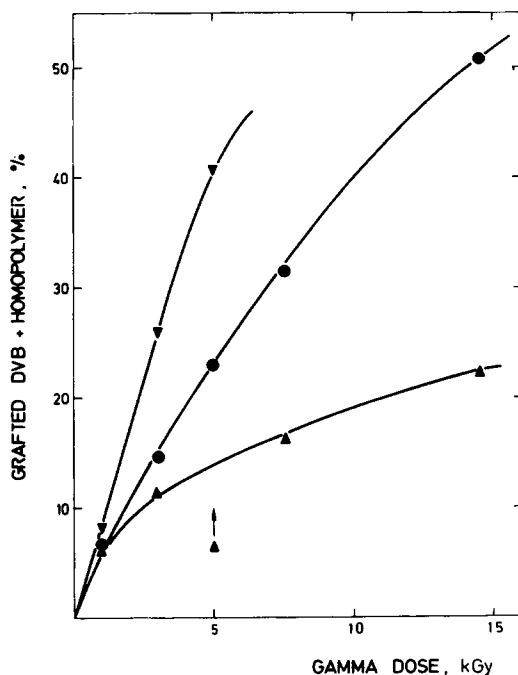


Fig. 2. Variation of extent of DVB grafting onto cotton fabric (nonextracted samples) with increasing irradiation dose and dose rate: (▼) 10 mGy/sec; (●) 0.27 Gy/sec; (▲) 1.73 Gy/sec.

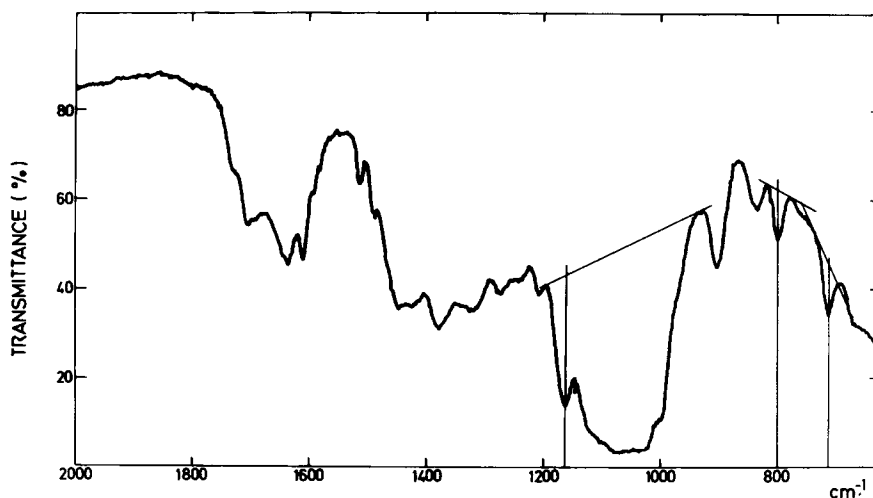


Fig. 3. Infrared absorption spectrum of mechanical mixture of cotton fabric (66%) and poly-DVB (34%).

(66 wt.%) and DVB polymer (34 wt.%) shown in Figure 3 served for comparison and for the selection of characteristic bands in the spectra of true copolymers. The band at 1610 cm^{-1} , the vinyl $\text{C}=\text{C}$ stretching, indicates the presence of DVB monomer since there have been no attempts at removing it. The spectra of DVB-cellulose copolymers are shown in Figures 4 and 5. The latter was obtained with a sample containing also DVB homopolymer. It was now possible to select characteristic bands in order to follow polymerization. These are the stretching

TABLE I
DVB Grafting Onto Cotton Fabric Previously Grafted With Styrene

Irradiation dose, kGy	Styrene grafting, %	Subsequent irradiation dose, kGy	Styrene + DVB grafting, %
1.0	5.0	0.2	6.85
1.0	5.0	0.5	7.94
2.5	10.9	1.0	18.37
5.0	25.5	1.0	34.00
5.0	25.5	3.0	53.80

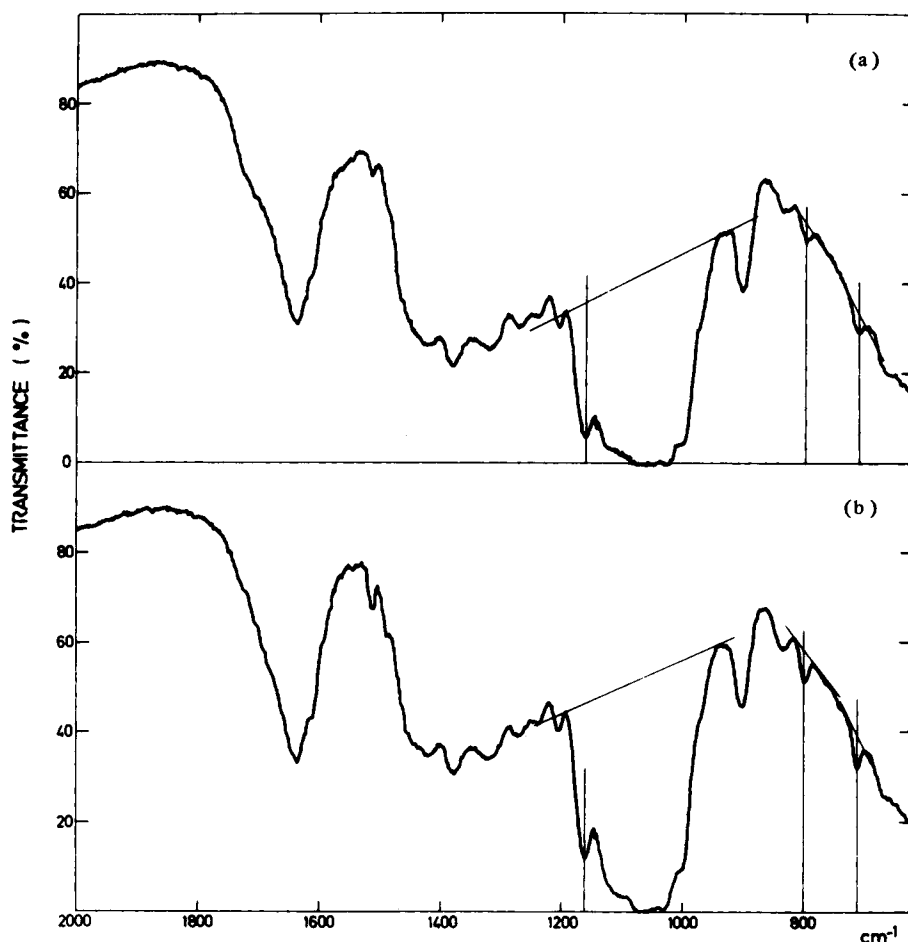


Fig. 4. Infrared absorption spectra of DVB graft onto cotton fabric. Weight gain of cotton samples was (a) 27.7% and (b) 37.7%.

bands of the cellulose C—O—C group at 1160 cm^{-1} , the aromatic CH group deformation at 832 cm^{-1} , and the deformations of aromatic ring at 798 and 712 cm^{-1} . The band at 905 cm^{-1} is the superposition of a cellulose and a DVB band.

For the quantitative analysis of DVB grafting the cellulose band at 1160 cm^{-1}

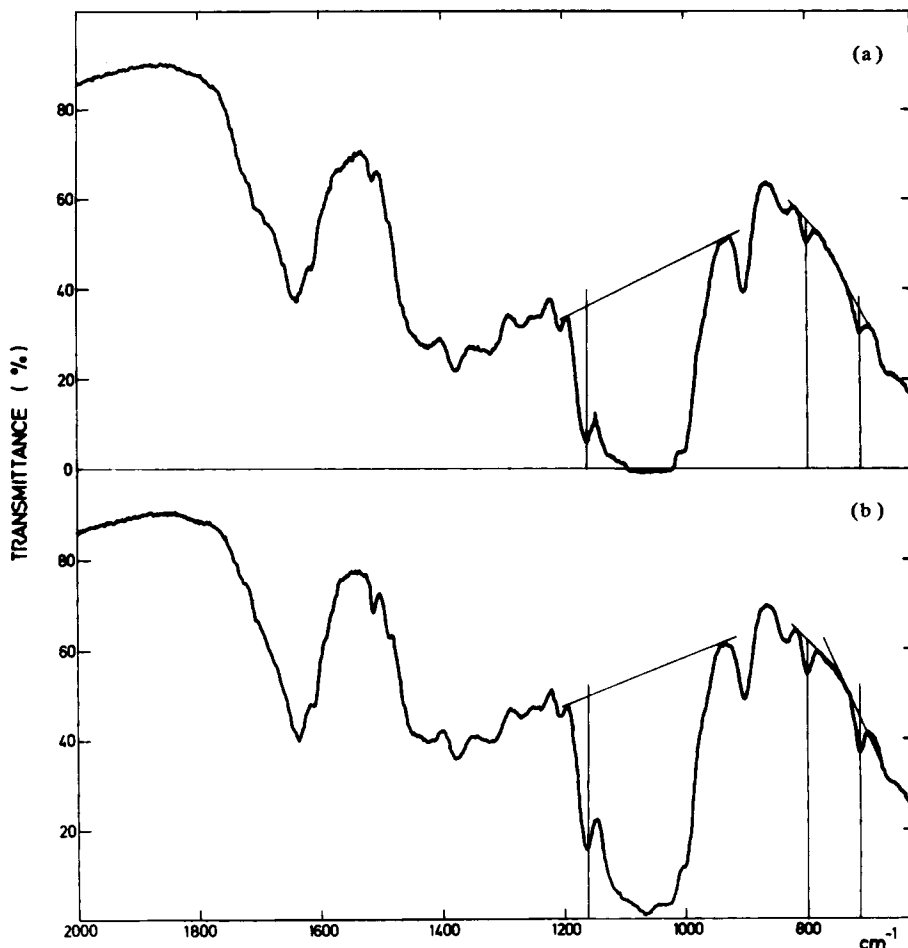


Fig. 5. Infrared absorption spectra of DVB graft onto cotton fabric (nonextracted samples). Weight gain of cotton samples was (a) 33.2% and (b) 50.8%.

and the DVB band at 798 cm^{-1} were selected. The former band decreases and the latter increases with the degree of polymerization. Another DVB band at 712 cm^{-1} can also be used instead of that at 798 cm^{-1} .

DISCUSSION

The results of DVB grafting onto cotton fabric have shown that whereas the extent of grafting increases with the irradiation dose up to 10–15 kGy, it depends considerably on the radiation dose rate. As already proved in other cases of grafting to cellulose⁴ for the same total radiation dose, the extent of DVB grafting decreases with the increase in the radiation dose rate.

Significant differences between the infrared spectra of the mechanical mixture of cellulose and DVB polymer (Fig. 3) and the spectra of the irradiated DVB–cellulose systems (Figs. 4 and 5) prove that the copolymerization of the two components occurred in the course of gamma irradiation. This is supported by a comparison of the relative intensities of the characteristic bands.

Applying the Beer–Lambert law and using the baseline method,¹⁰ we have

found that the absorbance of the cellulose band at 1160 cm^{-1} of the mechanical mixture (34.6% poly-DVB, Fig. 3) is 0.491 and that of the 798 cm^{-1} band is 0.082. The corresponding values for copolymer samples with the weight gain of DVB graft 27.7%, Figure 4(a), are 0.774 and 0.040, and for 37.7% gain of DVB graft, Figure 4(b), 0.602 and 0.056. The values for these two samples coalesce with the calibration straight line (the bands with no overlap¹⁰), but this was not the case with the mechanical mixture. In the case of samples with copolymer + DVB-homopolymer (Fig. 5), one notices a further decrease in the 1160 cm^{-1} band and an increase in the 798 cm^{-1} band as the DVB content increases to 33.2%, Figure 5(a), and 50.8%, Figure 5(b), weight gain of the total DVB. However, no definite conclusions about the type of bonding between copolymer and homopolymer can be made at this stage of investigation.

It is interesting to note that no significant changes in the band positions or relative intensities were noted in the IR spectrum of pure DVB polymer (not shown here), as compared to that of the cellulose-DVB copolymer. Consequently, it is not possible to determine the length of the DVB crosslinks and their positions on the cellulose chain on the basis of the present IR spectra only.

Somewhat unexpected results are presented in Table I, i.e., the cotton fabric previously grafted with styrene copolymerized DVB to a greater extent than the "pure" fabric. Thus, for instance, styrene-grafted fabric (weight gain 25.5%) copolymerized and additional 28% of DVB in the subsequent grafting at a radiation dose of 3 kGy, whereas for pure cotton fabric, according to the results given in Figure 1 at the same radiation dose, the extent of DVB grafting of only ca. 12% could have been expected. A possible explanation of the effect observed would be that the first grafting onto cotton tends to open up the morphological structure thereby exposing more of the surface area per unit weight of cellulose. Consequently, more sites for grafting were provided during the second (DVB) copolymerization. Another factor may be the higher extent of copolymerization of DVB monomer onto polystyrene side chains than onto pure cellulose.

References

1. J. C. Arthur, Jr., *J. Macromol. Sci. Chem.*, **A10**, 653 (1976).
2. T. J. Guthrie, *Polymer*, **16**, 134 (1975).
3. R. Teichman, *Faserforsch. Textiltech.*, **26**, 66 (1975).
4. P. W. Moore, *Rev. Pure Appl. Chem.*, **20**, 139 (1970).
5. M. Ishanov et al., *Uzb. Biol. Z.*, **16**, 17 (1972).
6. W. Bobeth, A. Mally, and J. Kulesa, *Faserforsch. Textiltech.*, **23**, 35 (1972).
7. H. Eschwey and W. Burchard, *J. Polym. Sci. Polym. Sym.* **53**, 1 (1975).
8. *Beilstein's Handbuch der Organischen Chemie*, V. Band, Springer-Verlag, Berlin, 1943, p. 414.
9. S. Trbojević-Gobac and M. Vlatković, *Tekstil*, **24**, 333 (1975).
10. V. J. I. Zichy, in *Laboratory Methods in Infrared Spectroscopy*, 2nd ed., R. G. J. Miller and B. C. Stace, eds., Heyden, London, 1972, Chap. 5.
11. L. J. Bellamy, *Infrared Spectra of Complex Molecules*, 3rd ed., Chapman and Hall, London, 1975.

Received June 29, 1978

Revised January 8, 1979