

Grafting on Cellulose Acetate

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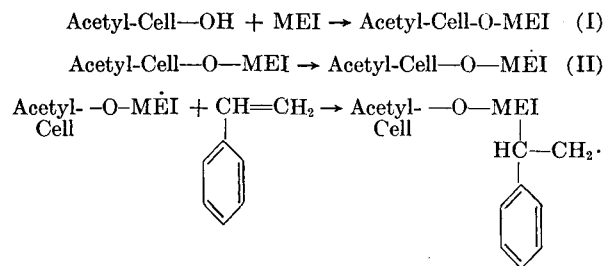
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Working on the possibility of modifying the properties of cellulose acetates, we have studied the grafting of styrene monomer on the cellulosic chain in several ways.

In the literature can be found a description of a process that presents analogies with one of our experiments, that is, the grafting of styrene on a mixed ester of cellulose, cellulose aceto-11-bromo-undecanoate.¹ A more recent reference is found in a review of possible ways of grafting monomers on natural polymers and their derivatives.²

These processes presume the use of a cellulose mixed ester of an unsaturated organic acid as main chain polymer, but we have succeeded in grafting the styrene on a cellulose ester of an aliphatic, saturated acid by introducing an unsaturated group in the cellulosic polymer through etherification.

It is known that ethylenimine (I) reacts with —OH groups of cellulose and with residual —OH groups of its derivatives.³⁻⁴ Then, starting from methacryloylethylenimine (MEI) it has been possible to introduce acrylic unsaturation in the cellulosic polymer and finally to graft the styrene thereon (II).



EXPERIMENTAL RESULTS

A. Grafting of Styrene on Cellulose Acetocrotonate and Cellulose Acetomaleate

The two mixed esters were prepared by the reaction of the anhydrides on commercial cellulose acetates of various acetyl contents (Hercules FM3 containing 56.8% acetic acid and Rhodistotoce tri-

acetate containing 61.0% acetic acid) by means of classical methods.⁹

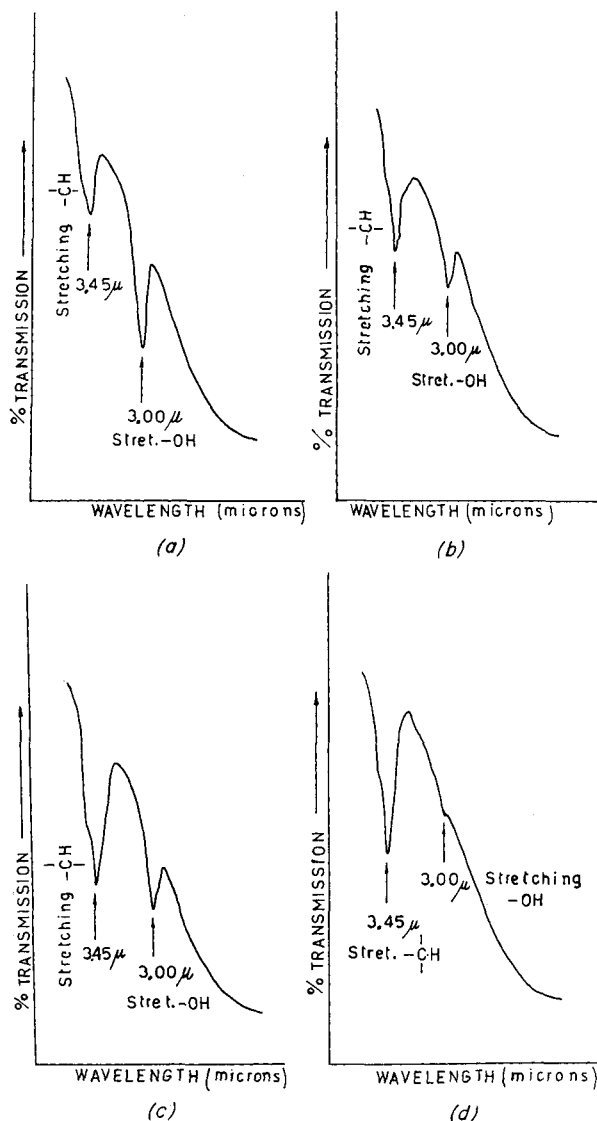


Fig. 1. Infrared spectra of cellulose esters: (a) cellulose acetate, acetic acid content 56.8%; (b) mixed ester of cellulose acetate and crotonate, acetic acid content 56.8%; (c) cellulose acetate, acetic acid content 61%; (d) mixed ester of cellulose acetate and maleate, acetic acid content 61%.

TABLE I

No.	Trunk polymer	Esterification				Grafting result	Infrared spectrum of product (Fig. no.)
		Acetic acid content, %	Catalyst	Anhydride	Analytical data, acid content, %		
1	Cellulose acetate	56.8	H ₂ SO ₄ , 0.2%	Crotonic	Crotonic, 6.5	Positive	2
2	"	56.8	ZnCl ₂ , 1%	Crotonic	Crotonic, 2.3	Positive	3
3	"	61.0	CH ₃ COONa, 2%	Maleic	Maleic, 1.7	Dubious; insoluble product	9
4	"	61.0	CH ₃ COONa, 2%	Maleic	Maleic, 1.7	Soluble fraction: positive. Insoluble fraction: band of maleic polymerization	4
5	"	61.0	CH ₃ COONa, 2%	Maleic	Maleic, 1.7	Soluble fraction: positive. Insoluble fraction: band of maleic polymerization	5
6	"	61.0	CH ₃ COONa, 2%	Maleic	Maleic, 1	Soluble fraction: positive. Insoluble fraction: band of maleic polymerization, 6% grafted polystyrene	6

TABLE II

No.	Trunk polymer	Addition			Grafting result	Infrared spectrum of product (Fig. no.)
		Acetic acid contents, %	MEI, % on cellulose acetate	Analytical data, N content, %		
8	Cellulose acetate	56.8	100	0.128	Positive	11
9	" "	56.8	5	0.153	Positive	12
10	" "	61.0	10	0.06	Dubious	13

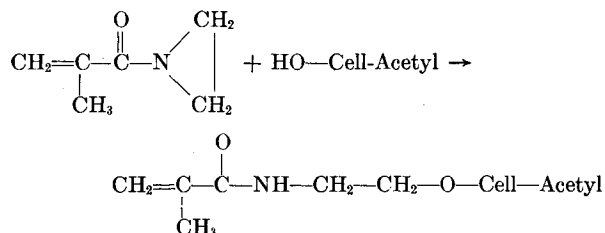
The mixed esters thus obtained were allowed to swell in ethylene chloride at 80°C., and then to react, at the solvent boiling point, with styrene monomer for several hours in the presence of benzoyl peroxide (Bz₂O₂).

The reaction mixture was precipitated in benzene and the product washed repeatedly with benzene in a Soxhlet extractor until all the free styrene homopolymer was removed.

The grafting was verified by infrared spectroscopy (Table I).

B. Grafting of Styrene on Cellulose Acetate Modified with Methacryloylethylenimine (MEI)

MEI was introduced into cellulose acetate through the reaction of the imine with a polymer solution in anhydrous methylene chloride at solvent boiling point (39.8°C.) for several hours.

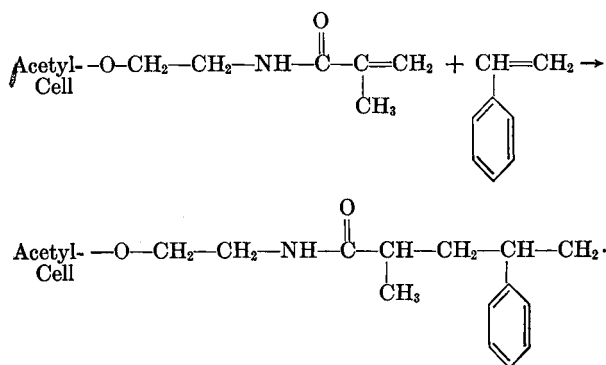


The modified acetate was precipitated with methyl alcohol, in order to remove the MEI excess, washed repeatedly with CH₃OH, and finally dried.

The reaction of the polymer was verified both by infrared spectroscopy and by chemical methods (micro-Kjeldahl nitrogen determination) (Table II).

Then we grafted on the styrene, allowing the monomer to react for several hours with modified cellulose acetate dissolved in CH₃COCH₃ at the

solvent boiling point and in the presence of added Bz_2O_2 .



The product was purified and determined as done previously in (A).

DISCUSSION OF RESULTS

For experiments of group A the infrared spectra of the mixed esters of cellulose acetate and aceto-crotonate or acetomaleate were investigated on a Perkin-Elmer Model 112 spectrometer in the $-OH$ stretching vibration zone at 2.9μ .

We observed a continuous decrease in intensity of this vibration on introduction of the maleic group or the crotonate one into the cellulose acetate. This variation in intensity is proportional to the degree of substitution of the maleic or crotonic groups, whose quantity varies between 1.5 and 6.5%.

At up to wavelengths of 15μ we could detect no other vibrations attributable to the modification,

perhaps because the per cent of introduced product is too low in comparison with cellulose acetate (Fig. 1).

In our experiments with cellulose acetocrotonate, the infrared spectra (Figs. 2 and 3) show two absorption bands of low intensity at 13.25 and 14.35μ that we attribute to the out-of-plane vibration of H atoms of the monosubstituted benzene nucleus in the grafted styrene. We can exclude the presence of styrene monomer because if this were the case, the vibrations of the aromatic nucleus would be seen at 12.9 and 14.35μ .

The strong intensity of observed bands allows an approximate quantitative evaluation of the examined product. Whiffen and Thompson,⁸ for instance, elaborated a method for the quantitative analysis of cresylic acid based on these bands.

In the same way we can examine the experiments with cellulose acetomaleate. The infrared spectra (Figs. 4, 5, and 6), show the same characteristic absorption of grafted styrene.

Besides the qualitative analysis by infrared spectroscopy, a quantitative determination of the grafted polystyrene was made on the basis of the total saponification of the grafted cellulosic ester and on the difference in weight between the initial product and the components of cellulosic ester after the saponification.

Thus the analysis of sample 7 gave about 6% of grafted polystyrene; this value agrees with the evaluation made from the intensity of the infrared bands.

For the quantitative evaluation, we chose the

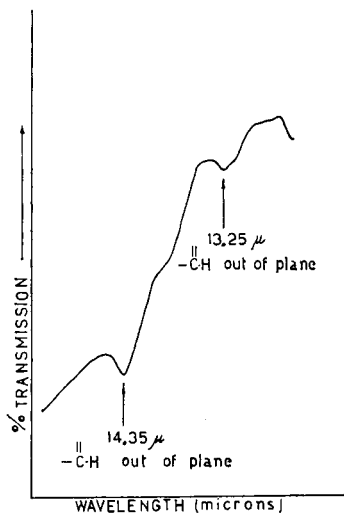


Fig. 2. Infrared spectrum of polystyrene grafted on cellulose acetate-crotonate.

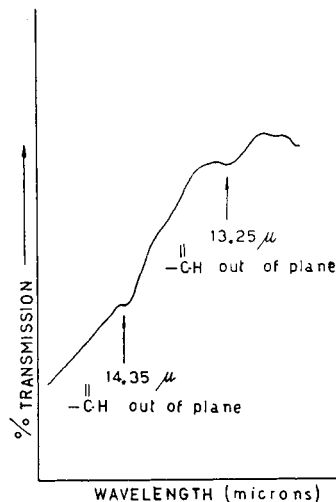


Fig. 3. Infrared spectrum of polystyrene grafted on cellulose acetate-crotonate.

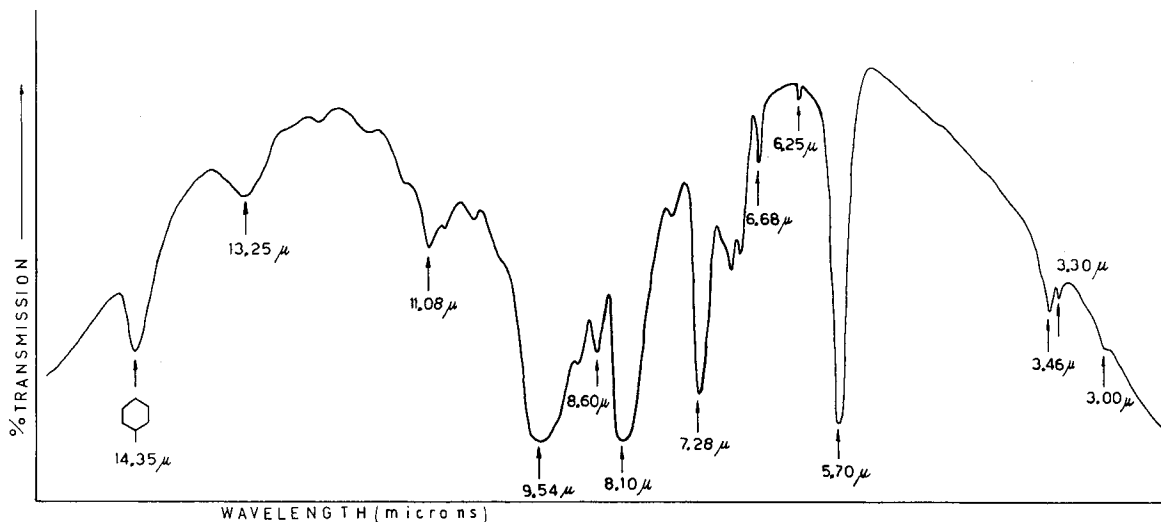


Fig. 4. Infrared spectrum of polystyrene grafted on cellulose acetate-maleate. Assignment of bands: 3.00μ , —O—H stretching; 3.30μ , aromatic C—H stretching; 3.46μ , C—H stretching; 5.70μ , ester C=O stretching; 6.25μ and 6.68μ , skeletal in-plane C=C (aromatic); 7.28μ , C—H deformation; 8.10μ , —C—O— deformation; 8.60μ , —C—O—H deformation; 13.25μ and 14.35μ , out-of-plane —C—H deformation.

absorption band at 14.35μ and followed the baseline method. The value thus obtained was 5.7%. As a control we observed the spectrum (Fig. 7) of a simple mixture of polystyrene and cellulose acetate of which the polystyrene percentage was known to be 6%.

It is interesting to note that in each sample, after the grafting, it was possible to separate a fraction that was not soluble in solvents of cellulose acetate. This fraction was very small if the grafting was made in a dilute solution, but increased with in-

creasing initial concentration of the mixed ester.

This insolubilization might be indicative of crosslinking of the main chain polymer by polystyrene chains built up between two maleic unsaturations of two different cellulosic chains. On the other hand, inspection of the infrared spectra shows that in the insoluble fraction there is no vibration that can be attributed to polystyrene. Furthermore a blank, i.e., an experiment made under the same conditions of grafting but without the styrene monomer, yielded an insoluble product that shows a quite similar infrared spectrum (Fig. 8).

By inspecting this and other spectra of the insoluble fraction, we noted that an absorption band appears at 14.39μ while the =C—H out-of-plane vibrations of the aromatic ring are not visible. Therefore, we think that in our experiment a polymerization, or a simple dimerization, of the maleic groups occurred.

In fact, in other experiments previously made with maleic derivatives, an absorption band appears at 14.39μ that increases in intensity with reaction temperature above 100°C .

In order to illustrate this, we show for the comparison that portion of the infrared spectrum that concerns the band in question for cellulose acetate-maleate (Fig. 9).

Let us remember that maleic anhydride shows a weak absorption band exactly in this zone (Fig.

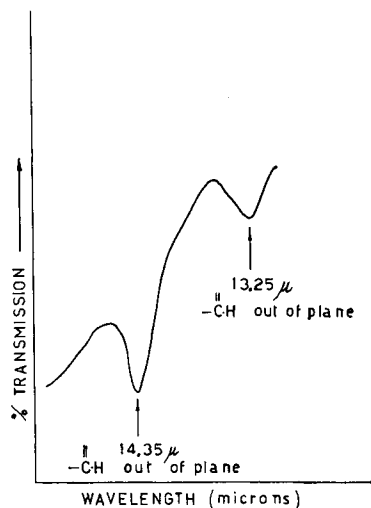


Fig. 5. Infrared spectrum of polystyrene grafted on cellulose acetate-maleate.

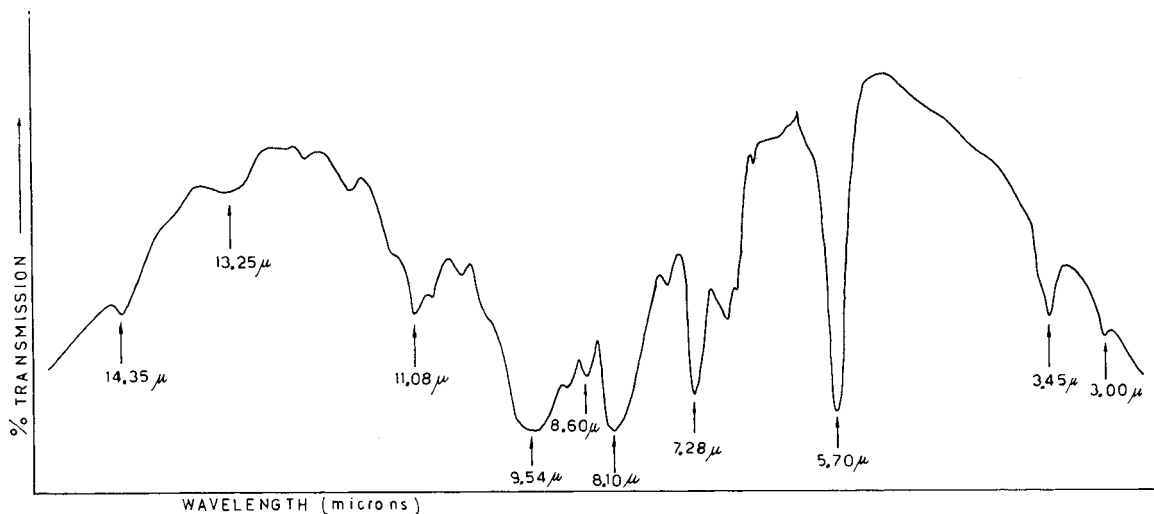


Fig. 6. Infrared spectrum of polystyrene grafted on cellulose acetate-maleate. Assignment of bands: 3.00μ , —O—H stretching; 3.45μ , —C—H stretching; 5.70μ , ester C=O stretching; 7.28μ , —C—H deformation; 8.10μ , —C—O— deformation; 8.60μ , —C—O—H deformation; 13.25μ and 14.35μ , out-of-plane —C—H deformation.

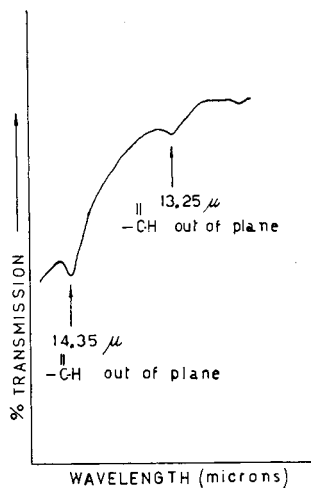


Fig. 7. Infrared spectrum of mixture of polystyrene (6%) and cellulose acetate.

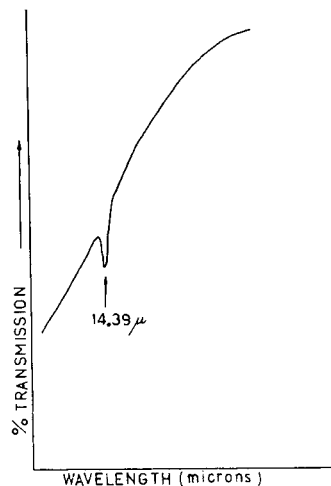


Fig. 9. Infrared spectrum of insoluble product obtained on grafting of styrene on cellulose acetate-maleate.

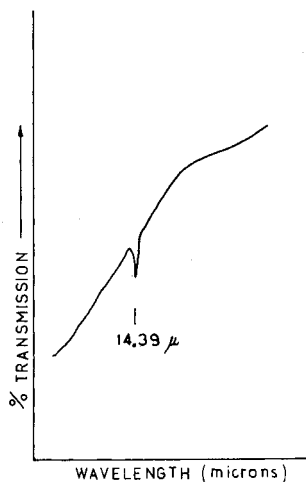


Fig. 8. Infrared spectrum of blank without styrene.

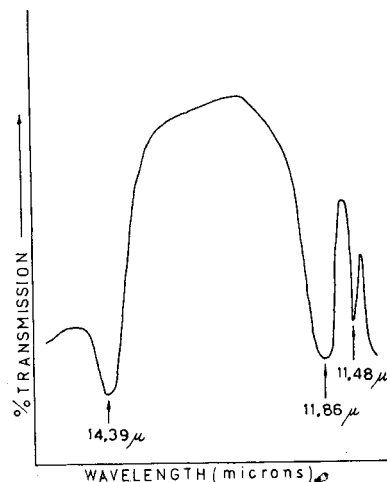


Fig. 10. Infrared spectrum of maleic anhydride.

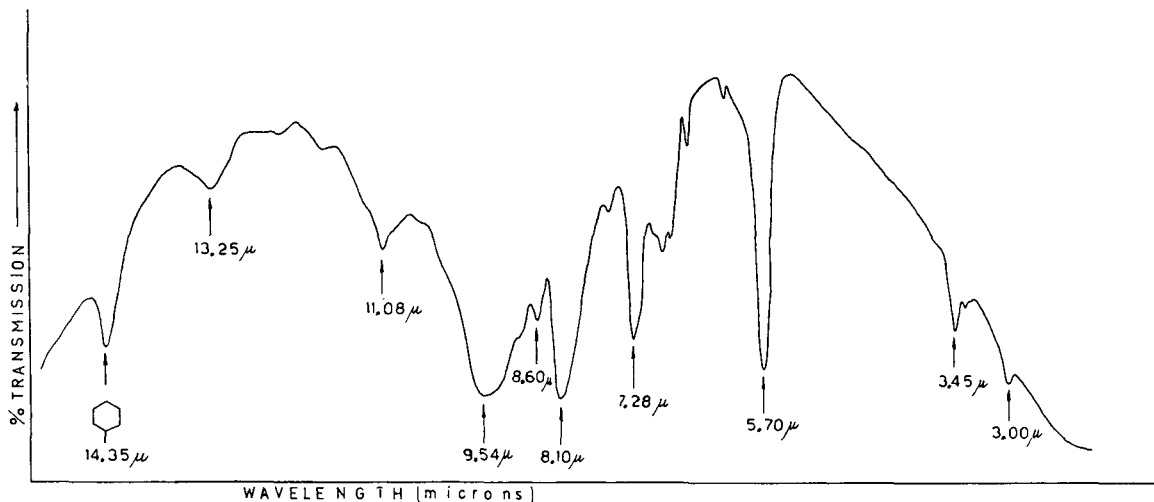


Fig. 11. Infrared spectrum of polystyrene grafted on cellulose acetate modified with MEI. Assignment of bands: 3.00μ , —O—H stretching; 3.45μ , —C—H stretching; 5.70μ , ester C=O stretching; 7.28μ , —C—H deformation; 8.10μ , —C—O— deformation; 8.60μ , —C—O—H deformation; 13.25μ and 14.35μ , out-of-plane —C—H deformation.

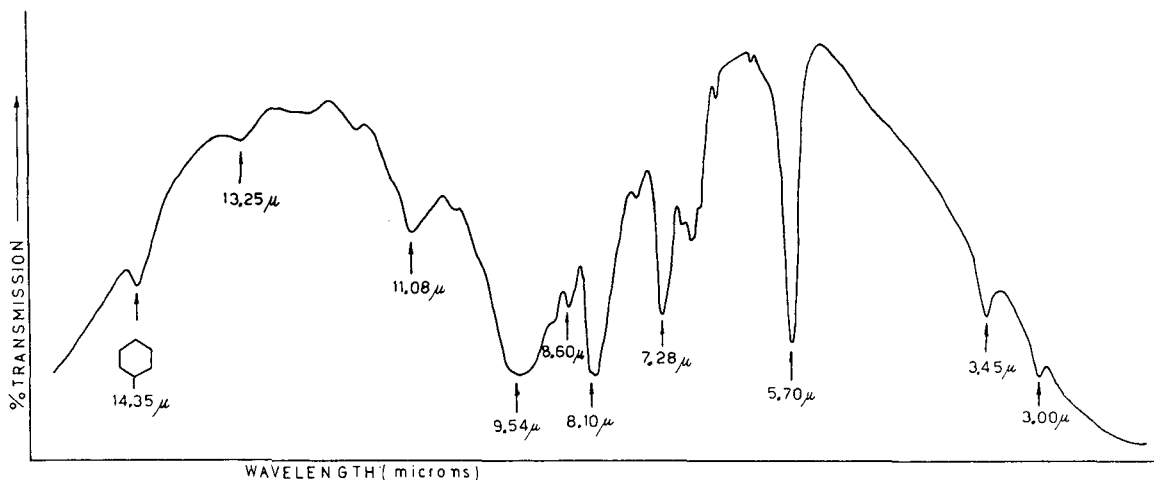


Fig. 12. Infrared spectrum of polystyrene grafted on cellulose acetate modified with MEI. Assignment of bands: 3.00μ , —O—H stretching; 3.45μ , —C—H stretching; 5.70μ , ester C=O stretching; 7.28μ , —C—H deformation; 8.10μ , —C—O— deformation; 8.60μ , —C—O—H deformation; 13.25μ and 14.35μ , out-of-plane —C—H deformation.

10); however, on repeated extractions of the insoluble fraction with the usual solvents, no maleic anhydride was isolated.

On another series of experiments (group B), inspection of the infrared spectra (Figs. 11 and 12) confirms the presence of grafted styrene nucleus; the spectrum in Figure 13 does not emphasize the vibrations of the monosubstituted benzene ring unless the thickness of examined film gets much higher. This fact indicates that very little styrene has been grafted to the mixed ester of cellulose acetate with MEI. Quantitative analysis of samples

8 and 9 certifies, on the contrary, styrene contents of 8 and 6%, respectively.

It should be noted that with a cellulose acetate with a high acetic acid content (about 61.0%) the reactivity of MEI appears to be lower than that of maleic anhydride. Therefore we were not able to introduce more acrylic unsaturated groups in the cellulosic polymer in order to emphasize the grafting of styrene. At no time in these experiments was an insoluble fraction of cellulosic ester noted, even though this would have been more reasonable with an acrylic compound than with maleic anhydride.

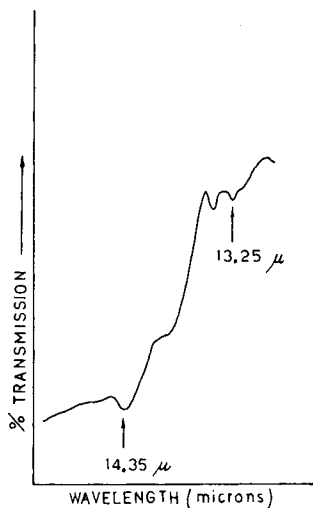


Fig. 13. Infrared spectrum of polystyrene grafted on cellulose acetate modified with MEI.

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Synopsis

The possibility of grafting and polymerizing unsaturated monomers, styrene chiefly, on cellulose acetates of different acetyl contents after introduction of an unsaturated group in the cellulosic ester was studied. This group was introduced by further esterification with unsaturated anhydrides (maleic and crotonic) or by etherification with methacryloyl-ethylenimine. The samples, examined by infrared spectrometry and by analytical methods, show a maximum of 6-8% of grafted styrene with respect to the cellulosic ester.

Résumé

On a étudié la possibilité de greffer et de polymériser des monomères nonsaturés, principalement le styrène, sur des acétates de cellulose qui ont un taux d'acétyle variable. Ceci a été fait après avoir introduit un groupe nonsaturé dans l'ester cellulosique. Ce groupe a été introduit par estérification avec des anhydrides nonsaturés (maléique et crotonique) ou par éthérification avec la méthacryloyléthylèneimine. Les échantillons, examinés par spectrométrie infra-rouge et par des méthodes analytiques, montrent un maximum de 6-8% de styrène greffé par rapport à l'ester cellulosique.

Zusammenfassung

Die Möglichkeit, ungesättigte Monomere, hauptsächlich Styrol, auf Celluloseacetat mit verschiedenem Acetylgehalt nach Einführung einer ungesättigten Gruppe in den Celluloseester durch Polymerisation aufzupropfen, wurde untersucht. Die ungesättigte Gruppe wurde durch weitere Veresterung mit ungesättigten Anhydriden (Malein- und Crotonsäureanhydrid) oder durch Verätherung mit Methacryloyläthylenimin eingeführt. Die Proben zeigen nach dem infrarot-spektrographischen Befund und nach analytischen Methoden einen Maximalgehalt an aufgepropftem Styrol von 6-8% bezogen auf den Celluloseester.

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