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Preparation and properties of polymers of carboxylated polybutadiene containing sucrose

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SYNOPSIS

This paper describes the attachment of sugar (sucrose) to low molecular weight carboxylated polybutadiene (esterification) to produce a new class of synthetic polymers. The products were characterized by I.R. and N.M.R. spectroscopy. Their thermal and thermooxidative characteristics are discussed from DSC and TGA in nitrogen and air. The polyurethanes obtained were studied.

INTRODUCTION

The polyfunctional structure of sucrose could be useful to build up molecules that cannot be produced by a petrochemical process. Previous papers report about the synthesis of mono or diesters of sucrose. Some of these diesters with residual vinyl groups were capable to polymerize to a product containing a significant concentration of OH groups (1-4). Other works inform about the unsuccessful synthesis of polyether of poly(vinyl alcohol) and sucrose (5-6). We have herein synthesized sucrose polyesters using a carboxylated polybutadiene.

EXPERIMENTAL

The copolymers containing sucrose were synthesized from butadiene-acrylic acid copolymers and polybutadiene carboxylates.

Prepolymes I and II were synthesized by bulk polymerization using 1,3-butadiene and acrylic acid and benzoyl peroxide catalyst (7).

Prepolymer III was commercial Butarez.(Phillips Petroleum Co.)

To introduce sucrose, the carboxyl groups of pre-polymers I, II and III, were reacted with thionyl chloride using dry benzene solvent in an ice bath for two hours. The product was dried and then reacted at room tempeature with a solution of sucrose in dry DMF and 0.1% of Et_3N.

The samples were purified by fractional precipitation using benzene solvent and methanol nonsolvent, and by GPC.

Determination of the carboxyl groups was carried out by titration using potassium hydroxide in a methanol solution (0.1 N) and thymol blue indicator. The determination was made before and after esterification, thus permitting to know the approximate percent conversion.

TGA and DSC were performed at the Centro de Investigaciones y Desarrollo de Santa Fé, ARGENTINA.

IR and ^{1}H-NMR spectra were obtained on a Nicolet 5 SXC spectro-

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photometer, FT-IR spectrometer and Varian T-60 spectrophotometer, respectively.

Polymers V and VI were silylated using anhydrous pyridine solvent and Tri-Sil Concentrate (Pierce) silylation reagent. They were kept for two hours at 40-50ºC. Trietylamine was used as catalyst.

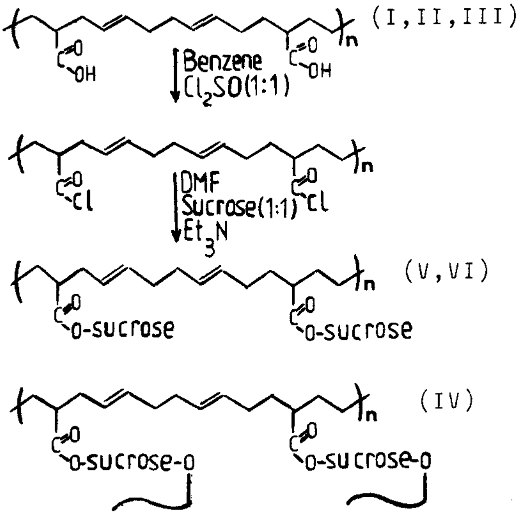
The products were dried and dissolved in CCl_4 to be analyzed by ^{1}H-NMR spectrometry.

Polymers V and VI were reacted with toluene diisocyanate (TDI) so as to obtain polyurethanes. Thus, each polymer was dissolved in dry benzene, TDI was added (1:1), and at refluxed for two hours. The products were dried and yellowish foamy products were obtained.

RESULTS AND DISCUSSION

The new resins obtained were synthesized from prepolymers with different carboxyl content as shown in Figure 1.

FIGURE 1: SCHEME OF SYNTHESIS OF SUCROSE CONTAINING POLYMER.



Results are summarized in Table 1.

TABLE 1: Equivalent contents of reactants and products.

Starting Polymer	eq.-COOH base polymer	eq.-COOH product	conversion %	Characterization of product
Butadiene acrylic acid	0.16/100 gr	0.062/100	61	insoluble - IV
Butadiene acrylic acid	0.08/100 gr	0.028/100	65	soluble - V
Terminal carboxyl Polybutadiene	0.04/100 gr	0.024/100	43	soluble - VI

Two of the products obtained (V and VI) were transparent yellow resins, soluble in THF, benzene, o-di-Cl-benzene, CCl_4, $CHCl_3$ and DMF. The third product (IV) was a white viscous resin insoluble in common solvents.

Table 2 summarizes the swelling indexes found (8).

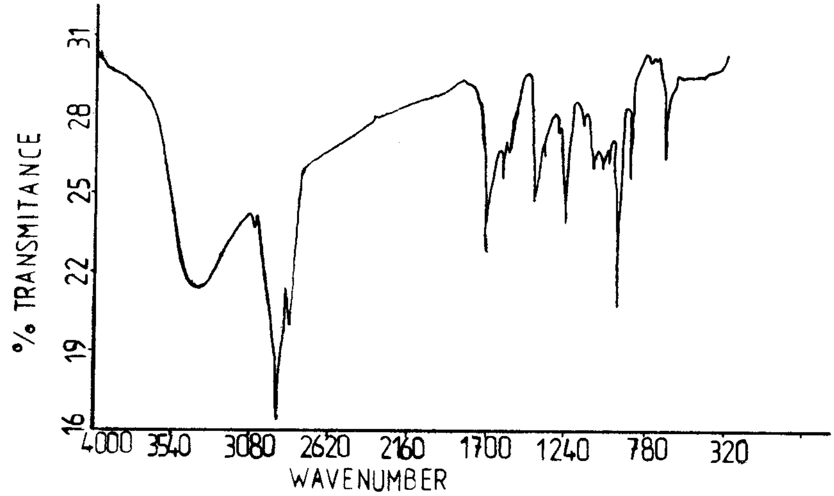
TABLE 2: Swelling Indexes of product IV.

Solvent	Index	Solvent	Index
O-di-Cl Benzene	7.89	Carbon Tetrachloride	1.86
Cl-benzene	4.76	Water	1.45
Toluene	4.55	Petroleum ether	1.31
Ethanol	1.98	Acetone	1.17

I.R. SPECTROSCOPY

The bands of the IR spectra were assigned as follows: the band atributable to the presence of the carboxylated polybutadiene chain at 715 cm^{-1} (1,4-cis addition); 911 cm^{-1} (1,2-vinyl addition); 996 cm^{-1} (1,4-trans addition); 1438 cm^{-1} ($-CH_2$ olefinic); 1638 cm^{-1} (-C= -non-conjugated); 1700-1720 (-C=O acid and ester); 2800-3100 cm^{-1} (-CH and =CH-); 3300-3600 cm^{-1} (-OH). Between 1050 and 1100 cm^{-1} we found a small band atributable to the -C-O-C bond.

FIGURE 2: I.R. SPECTRUM OF POLYBUTADIENE WITH SUCROSE.



^{1}H-NMR SPECTROSCOPY

The following resonances were found in the ^{1}H-NMR spectra: between $\delta = 5.70$ and 5.00 attributable to the vinylic protons of the 1,2 and 1,4 butadiene addition; between $\delta=2.4$ and 1.00, the allylic protons -CH and $-CH_2-$ from the rest of the hydrocarbon chain.

In products with high conversions the protons corresponding to the sucrose resonated between $\delta = 4.80$ and 3.10. The -OH group was found between $\delta = 3.00$ and 2.40, depending on the concentration.

Products which showed the absence of sucrose by ^{1}H-NMR spectroscopy were silylated. A new peak at $\delta = 0.40$ to 0.0 corresponding to the methylic protons $(-Si(CH_3)_3)$ was observed. For comparison prepolymers II and III were also silylated. In this case, the peak corresponding to the methylic protons was very small.

THERMAL ANALYSIS

Polymers containing sucrose showed good thermal and thermo-oxidative stability. The results obtained are summarized in Table 3.

According to DSC curves, two exotherms are present in polymers IV, V and VI. The first one is sharp and appears between 145º and 150ºC; the second one is broad and of higher intensity than the former, is between 300º and 400ºC. The thermochemical processes that justify the presence of such peaks are under study.

An endotherm that appears between 430-450ºC is assigned to the thermal degradation of the polymer chain.

FIGURE 3: ^{1}H-NMR SPECTRUM OF POLYBUTADIENE CONTAINING SUCROSE.

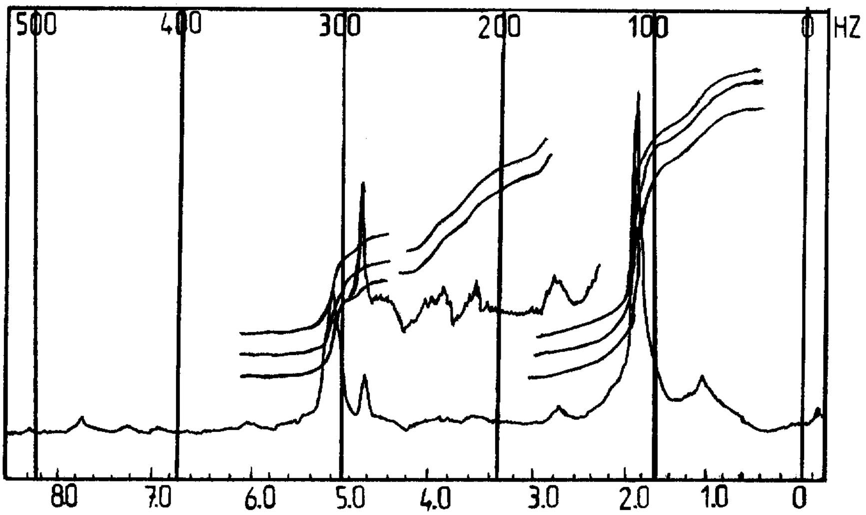


TABLE 3: T.G.A.

	POLYMER IV	POLYMER V	POLYMER VI
Initial temperature (ºC) of N_2 decomposition	300	355	300
Initial temperature(ºC) O_2 decomposition	400	405	400
Temperature of higher (ºC) % of N_2 decomposition	458	445	465
Temperature of higher (ºC) % of O_2 decomposition	445	430	450

CHARACTERISTICS OF POLYURETHANES

The polyurethanes obtained were yellow and insoluble in methanol and ethanol. They were sparingly soluble in THF, benzene, o-di-Cl- benzene and toluene with a high degree of swelling. IR spectroscopy showed the following bands characteristic of the urethane group: 2272 cm^{-1} (-NCO); 1539, 1710 and 3294 cm^{-1} (R-NH-C-O-). The other bands observed in the spectrum have been assigned above.

CONCLUSION

Polymers with pendant carboxyl groups were conveniently converted into poly-sugars with varying degrees of esterification. Higly esterified products were "gels" with different degrees of swelling, but poly-sugars with low degrees of esterification were soluble.The products showed good thermal and thermo-oxidative stability.

ACKNOWLEDGEMENT

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