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^{13}C-NMR Spectroscopy

^{13}C NMR Study of the Structure of the Hydrogel Polyester of Sucrose Methacrylate (Sucro-Gel H-70)

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SUMMARY

A ^{13}C NMR study of four samples of poly(sucrose methacrylate) differing in molecular weight and degree of crosslinking was performed to determine their structure. It was concluded that Sucro-Gel H-70 polymer consists mainly of monomer units of isomeric monoesters principally esterified in C6 C6´ C4 position and forming atactic helical chains with some crosslinks due to the presence of substituted monomer units.

INTRODUCTION

With the development of ^{13}C NMR spectrometers, which operate at high magnetic fields and in the pulse Fourier transform mode, a fundamental tool for structural and conformational studies is available (1). We think that the application of this technique could give much information about the structure of Sucro-Gel H-70, a polymer with a polymethacrylic-sucrose ester structure, previously synthesized by us (2).

EXPERIMENTAL

All polymers were synthesized as previously described (2) through transesterification. Sucrose was dissolved at 75ºC/85 mmHg in dry N,N-dimethylformamide; Sodium methoxide solution was added below the surface of the sucrose solution. Then methyl methacrylate (MMA) dissolved in N,N-dimethylformamide (DMF) was dropped from a pressure-equalising dropping funnel. Table 1 shows the relation of sucrose/MMA added to yield the four polymers made.

The reaction was maintained under these conditions for 3 hours. DMF was then removed under reduced pressure to yield a viscous, nearly colourless and transparent product consisting of a mixture of mono and polyfunctional methacrylic esters.

The ratio of mono to polyfunctional ester depends on the mole ratio of sucrose/methyl methacrylate.

The radical polymerization of these sucroester mixtures yield four different types of polymers (3) with different solvation character: S_{12}, S_5, S_4 and Si (Sucro-Gel H-70) as shown in table 1.

Table 1. Conditions and results of the preparation of different polymers (reaction time: 3h.)

Polymer	S_{12}	S_5	S_4	Si Sucro-Gel H-70
Solubility in water a)	+++	++	+	insoluble
Mole ratio Suc./MMA	1:1	1:1,5	1:2	1:3
Polymerization conditions	T:90ºC	UV. irrad at r.t. b)	UV. irrad at r.t. b)	T: 90ºC

a) +++: Most soluble; +: less soluble ($\bar{M}w$= 450.000); ++: intermediate solubility ($\bar{M}w$= 40.000)
b) r.t.: room temperature.

The polymers S_{12} ,$S_5$and S_4 are entirely soluble in water, DMF and DMSO The most soluble polymer was S_{12}. The solubility of the others decreases in the order given, S_i being insoluble in all solvents as well as in water, DMF and DMSO where a swelling was observed.

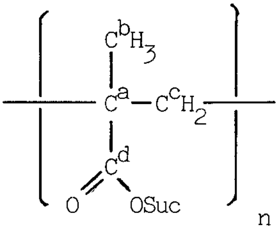
The soluble polymers were purified by fractional precipitation and centrifugation using water as solvent and acetone and methanol alternately as non-solvents. This process was repeated until the presence of sucrose was not observed by TLC in the supernatant.

The insoluble polymer, Sucro-Gel H-70, was purified by Soxhlet extraction for two days . The molecular weight of polymers S_5 and S_4 was determined by GPC.

Sucrose, the soluble polymers S_{12} ,S_5 ,S_4 and the insoluble Si, were analyzed on a Bruker PFT instrument operating at 50,31 MHz. The soluble polymers were dissolved in D_2O and the chemical shifts were expressed in ppm using DMSO (39,5 ppm) as internal reference.

RESULTS AND DISCUSSION

Figure 1. (E) shows the ^{13}C NMR spectrum of Sucro-Gel H-70 .The 12 peaks corresponding to the carbon atoms of the sucrose units in the macromolecule are present and can be identified according to previous assignments (4). This spectrum should also contain signals due to the carbon atoms of the methacrylic ester units at the following approximate positions:



δ (C^a): 52- 53 ppm
δ (C^b): 22- 27 ppm
δ (C^c): 62 ppm
δ (C^d): 177-180 ppm (5)

C^c is not observed since it appears in the region of the sharp peaks of sucrose carbons. Broad peaks appear at about 20 and 45 ppm which are assigned to C^b and C^a, respectively.

Figure 1. ^{13}C NMR comparative study of sucrose and various sucrose-free polymers

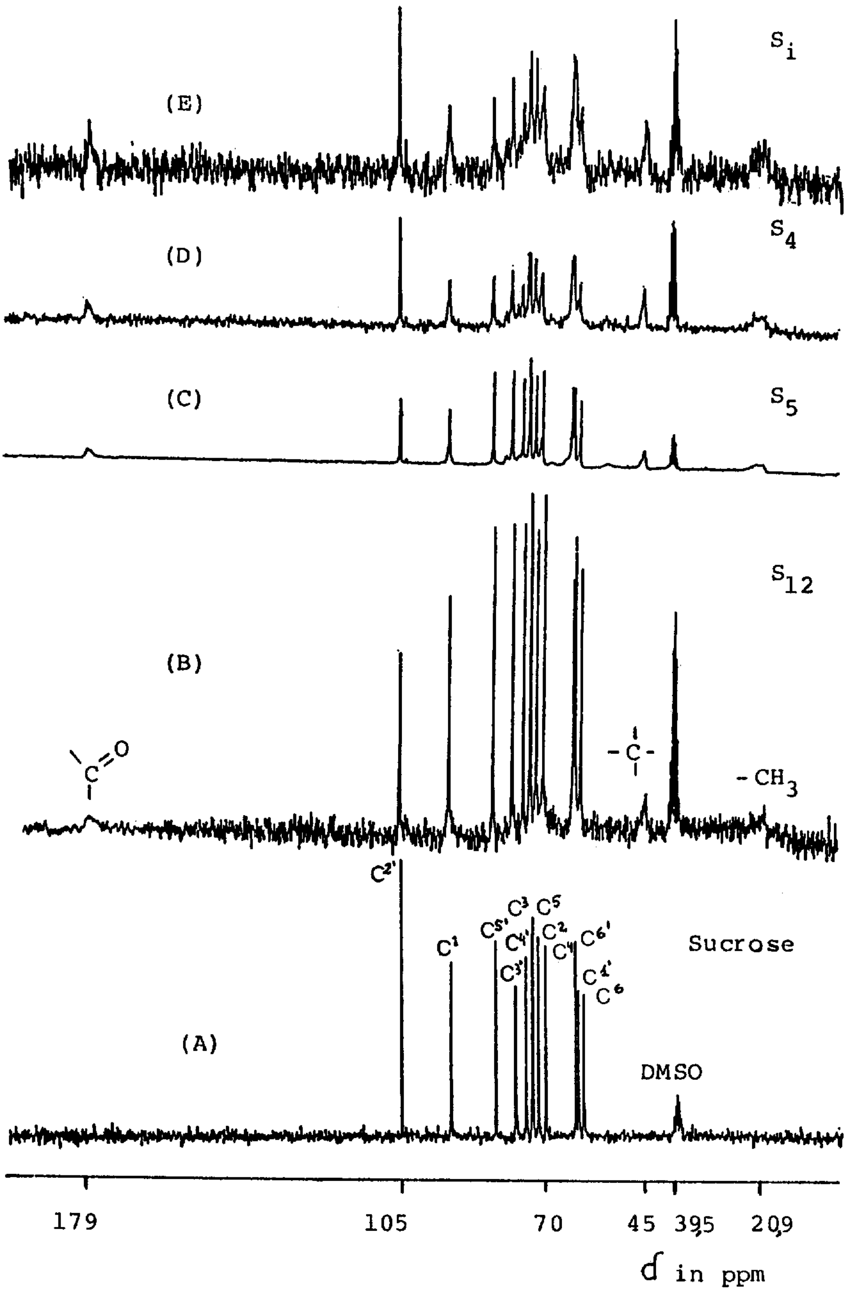


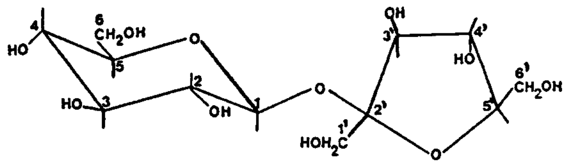
Table 2. Chemical shifts in the ^{13}C NMR spectra of sucrose and polyester of methyl methacrylate with sucrose (Suc).

	C^1		C^2	C^3	C^4		C^5	C^6		$C^{1'}$	$C^{2'}$		$C^{3'}$		$C^{4'}$		$C^{5'}$	$C^{6'}$		C^a	C^b	C^d
Sucrose	93,44		72,47	74,00	70,72		73,77	61,67		62,95	105,05		78,03		75,42		82,79	63,67				
S_{12} a)	93,50		72,53	74,06	70,81		73,84	61,74		63,08	105,09		78,21		75,59		82,81	63,69		46,14	17,47	179,87
$Suc-S_{12}$	-0,06		-0,06	-0,06	-0,09		-0,07	-0,08		-0,13	-0,04		-0,18		-0,17		-0,02	-0,03				
S_5 b)	93,46		72,49	74,04	70,78	70,01	73,80	61,72	62,29	63,06	105,06	103,72	78,19	79,64	75,57	76,66	82,78	63,65	64,84	46,33	17,79	180,28
$Suc-S_5$	-0,02		-0,01	-0,03	-0,06	-0,29	-0,03	-0,05	-0,57	-0,11	-0,01	+1,34	-0,15	-1,45	-0,15	-1,09	0,01	0,02	-1,19			
S_4 c)	93,40	92,39	72,47	74,00	70,74	70,97	73,78	61,68	62,09	63,05	105,18		78,18	79,22	75,53	76,66	82,81	63,59	63,86	46,14	17,13	180,25
$Suc-S_4$	0,04	+1,00	0,00	0,00	-0,03	-0,23	-0,01	-0,01	-0,41	-0,10	-0,14		-0,15	-1,64	-0,11	-1,13	-0,03	+0,08	-0,27			

a) Most soluble fraction of polyester of sucrose

b) Medium soluble fraction

c) Less soluble fraction



The irregular multiplicity and line broadening of the signals indicates unresolved tacticity effects. Since this polymer is in a swollen state (not in solution) so that some peak broadening is to be expected.

Then, a comparative study between sucrose and different sucrose-soluble polymers was done to observe modifications in the ^{13}C NMR spectra of the polymers with respect to that of sucrose, e.g.,the position and degree of esterification. The expected modifications are based on:

The esterification of the hydroxyl group causes a characteristic downfield shift to the α-carbon signals and a chemical shift in the other direction of the β-carbon (6); the 8 hydroxyl groups of the sucrose molecule react selectively in transesterification and the primary alcohols are sterically more accessible in the general order: C6 OH$\simeq$C6´OH>C4 OH C1´OH>>OH in other positions (7); the transesterification method used by us leads predominantly to monoesters.

Table 2, summarizes the chemical shifts of the spectra (A) - (E) in figure 1. Generally, in the five spectra, the twelve signals assigned to the sucrose units and other peaks involving the carbons of the ester function, are observed. The more soluble the polymers, the more similar their spectra to that of sucrose. The chemical shifts of the principal peaks do not change significantly with respect to that of sucrose, however, some new peaks can be ascribed to substitutions in positions 6´,4,4´ and 3´. As a result of multiple stereochmical changes in the macromolecule a broadening of these peaks takes place. The downfield shifts of the peaks of C6, C6´ and C4 are in agreement with the expected ones, according to their specific reactivity, leading to monoesters in those positions. On the other hand, downfield shifts of the signals of C4´,C4 and C3 may be due to another esterification leading to diesters differing from the above or to esterification at C6 which modifyes the chemical surrounding and produces anisotropic effects (deduced by examining a molecular model).

This type of chemical shift displacements produced by anisotropic effects, are observed, e.g., in the signals C2´ (Spectrum (C)) and C1 (Spectrum (D)), which cannot be esterified. For this reason, these new peaks may be due only to anisotropic effects. It is remarkable that these chemical shift displacements occur upfield.

"Space Filling Models" by using Corey-Pauling-Koflum units shown in figures 2 and 3 for the triad formed by methacrylate-sucrose monoesters as monomer, suggest a helical structure involving methacrylic units with sucrose moieties attached to the backbone.

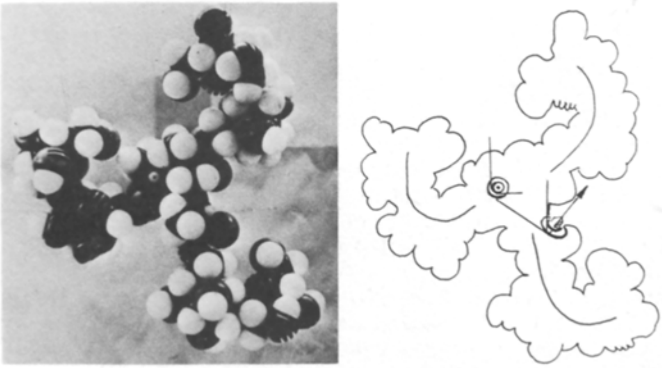


Figure 2. Triad of monomer units formed by sucrose methacrylate monoesters. The polymer grows in the directions shown above, forming a helical structure to which the sucrose moieties are attached

The participation of sucrose diesters would lead through branchy structures to networks. This observation is in line with the fact that, when the polymer contains more higher substituted ester units insolubility occurs and the spectra show peak broadening.

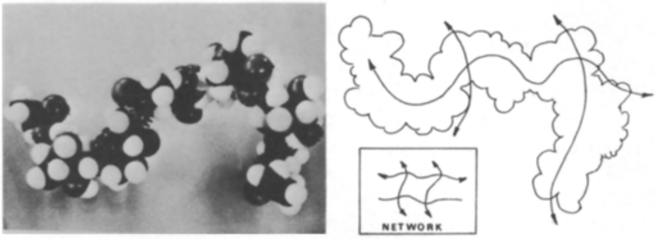


Figure 3 . Triad of monomer units formed by sucrose methacrylate diesters. The structure leads to a network, forming a type of macromolecular sieve.

This broadening of the ^{13}C NMR resonances of the polymers (gels) can be interpreted in terms of an immobilization of the polymeric chains due to bonding or crosslinking, as previously reported by Yokota for synthetic network polymers such as poly(N-vinylpyrrolidone) and poly(hydroxyethyl methacrylate) at low water contents. In this case, no chemical shift displacements were observed between the gel and non-crosslinked polymer solution (8).

CONCLUSION

Sucro-Gel H-70 consists of atactic polymer chains formed from isomeric monoester units and substituted principally in positions C6´,C6 and C4. Models suggest that the chain has a helical conformation with occasional crosslinks as a consequence of the participation of diesters. In the insoluble polymers these crosslinkings give rise to more rigid three-dimensional networks.

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