Stereochemical Studies on Poly(hydroxymethylene) and Poly(phenylvinylene glycol)

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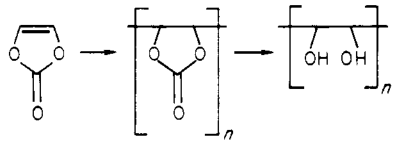
ABSTRACT: The free radical initiated polymerization of vinylene carbonate results in macromolecules that consist according to ^{13}C analysis of structural units characterized by both trans (*r*) and cis (*m*) configurations. These units are interlinked randomly by syn (*r'*) and anti (*m'*) connecting (junction) bonds. Within the temperature range of 3 to 160 °C an essentially constant value of 2 has been found for the ratio of the concentrations of trans units to cis units. Thus, with $\Delta(\Delta H^{\ddagger}) = 0$ and $\Delta(\Delta S^{\ddagger}) = 1.4$ eu, the preference for trans propagation appears to be the result of entropy factors. A configurational composition identical to that of the poly(vinylene carbonate) characterizes the poly(hydroxymethylene) which is obtained by hydrolysis of poly(vinylene carbonate). Hydrogen bonding effects may be mainly responsible for the influence of temperature and the nature of solvents on the spectral resolution for this polymer. For saturated solutions of LiCl in water or Me_2SO, resolution has been limited to triads even at 140 °C, whereas resolution of pentads has been feasible in hydrazine solution. An interpretation of the microtacticity has been possible by application of Bernouillian statistics. Poly(phenylvinylene glycol) obtained by hydrolysis of poly(phenylvinylene carbonate) has been investigated by both proton (270 MHz) and ^{13}C NMR analyses. Results of both are consistent with an atactic structure. There is evidence for the three possible triads entailing both threo and erythro structural units randomly placed syn and anti to each other. Though a slight preference for erythro propagation is indicated, the considerable extent of threo propagation observed, notwithstanding any conceivable intrasegmental phenyl–phenyl interactions, is rather characteristic of the kinetically controlled nature of free-radical polymerization.

Vinylene carbonate[1,2] (I) may be polymerized by free-radical initiation to high molecular weight poly(vinylene carbonate) (II) which upon hydrolysis yields poly(hydroxymethylene) (III) (PHM). The preparation and polymerization of I and its conversion to PHM have been described previously.[2] The high propensity to both intra- and intermolecular hydrogen bonding of PHM has resulted in rather unusual combinations of properties for this polymer. Notably is its high hydrophilicity and insolubility in water and most common solvents. We have been interested in the microstructure of this polymer especially with respect to its stereochemical configuration. Although the polymerization and copolymerization behavior of vinylene carbonate have been well described in the literature,[2,3,6] no information regarding the stereochemistry of its polymerization has been available and no NMR study of poly(vinylene carbonate) or PHM has been reported. ^{13}C NMR has been proven a valuable tool in determining the microstructure of synthetic polymers.[7,8] Since the range of ^{13}C chemical shifts is rather large (δ 200) when compared to that of ^{1}H NMR (δ 10), the technique is indispensable when high-resolution H^1 NMR becomes impractical as it is in the case for PHM. In this report we present ^{13}C NMR data on the microtacticity of poly(vinylene carbonate) and PHM, and a discussion of the stereochemistry of these polymers. Poly(phenylvinylene carbonate),[10,11] a homologue of poly(vinylene carbonate), and the corresponding hydrolysis product, poly(phenylvinylene glycol), have also been examined by both ^{1}H and ^{13}C NMR with respect to their configurational structure.



Experimental Section

Monomers: **Vinylene carbonate** was synthesized from ethylene carbonate via photochemical chlorination to monochlorethylene carbonate using a modification for the reported procedure.[1,2]

Phenylvinylene carbonate was prepared from phenacyl alcohol and phosgene according to the literature procedure.[11] It was recrystallized three times from heptane to obtain >99% purity (GC): ^{1}H NMR (100 MHz) δ 7.5 (s, aromatic), 7.35 (s, vinyl).

Polymers. Poly(vinylene carbonate). Vinylene carbonate was polymerized by typical bulk polymerization or suspension polymerization techniques.[2] Di-*sec*-butylperoxy dicarbonate at 35/40 °C, AIBN at 60 °C, and di-*tert*-butyl peroxide at 100–160 °C were used as initiators.

Solid-state low-conversion (<10%) polymerization was done at −5 °C using ^{60}Co γ-ray initiation at 0.1 Mrad/h as described in the literature.[12]

Poly(hydroxymethylene). Poly(vinylene carbonate) was converted to poly(hydroxymethylene) by hydrazinolysis and alkaline- or base-catalyzed hydrolysis.

Phenylvinylene carbonate (4.8 g) was polymerized with *tert*-butyl perbenzoate (50 mg) as initiator at 90 °C in a sealed tube for 3 days. The yellowish clear polymer plug was ground to a powder, dissolved in Me_2SO, and precipitated in methanol: yield, 45%; η_{inh} (DMS) 0.28; IR (KBr) strong band at 1840 cm^{-1} (>C=O).

Poly(phenylvinylene glycol). Poly(phenylvinylene carbonate) (2 g) was added with stirring to 10 mL of anhydrous hydrazine maintained at 60 °C. The polymer dissolved yielding a clear viscous solution. The clear solution was heated for a period of 3 h and then precipitated in an excess of methanol. Absence of the (>C=O) band at 1840 cm^{-1} indicated complete hydrolysis.

Model Compounds. *cis*- and *trans*-4,5-Dimethyl-1,3-dioxolan-2-one[13] (*cis*- and *trans*-IVb). The cis isomer was prepared by transesterification of *meso*-2,3-butane diol with diethyl carbonate. The trans isomer was similarly prepared from *rac*-2,3-butanediol.

***cis*- and *trans*-4,5-Diphenyl-1,3-dioxolan-2-one[14] (*cis*- and *trans*-IVc).** The cis isomer was prepared by a transesterification reaction of meso hydrobenzoin with diethyl carbonate. The trans isomer was similarly prepared from *rac*-hydrobenzoin.

***meso*-1,4-Dibromo-2,3-butanediol (VI).** Erythritol (24.2 g) (V) was heated with 200 mL of 48% hydrobromic acid for 24 h with stirring. The dark solution so obtained was extracted with 1 L of ether. The ether extract was dried and the ether removed under reduced pressure. The crude material was recrystallized from cyclohexane: mp 135 °C (lit.[15] 135–137 °C); yield, 8.8 g (38%).

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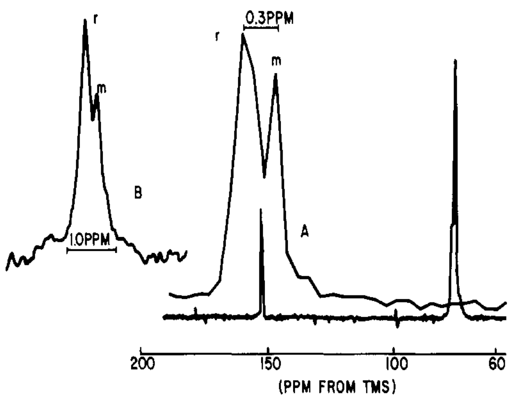


Figure 1. (A) ^{13}C NMR (20 MHz) of poly(vinylene carbonate) in Me_2SO-d_6 at 100 °C (S.W. = 4000 Hz), carbonyl expanded 40×. (B) 68-MHz spectrum (S.W. = 15000 Hz, 40× expanded carbonyl resonance). (η_{inh_6}) polymer: (A) = 1.0; (B) = 1.36.

***meso*-1,4-Dimethoxy-2,3-butanediol (VIII).** *meso*-1,4-Dibromo-2,3-butanediol (7.44 g, 0.03 mol) was dissolved in 20 mL of methanol and added dropwise to a solution of sodium methoxide (2.3 g of sodium) in 50 mL of methanol. The reaction mixture was refluxed overnight. The contents were carefully neutralized with concentrated HCl, and then the solvent was removed under reduced pressure. The residue was then extracted with ether (100 mL) to separate it from the inorganic salts. The ether solution was dried and concentrated under reduced pressure. The crude oily product was distilled at 115 °C (10 mm Hg): yield, 3 g (60%); H^1 NMR (60 M Hz) δ 3.4 (s, OCH_3), 3.6 (m, OCH_2, OCH), 4.7 (OH).

***cis*-4,5-Bis(methoxymethyl)-1,3-dioxolan-2-one (*cis*-IVa).** *meso*-1,4-Dimethoxy-2,3-butanediol (3 g, 0.02 mol) was heated with diethyl carbonate (10 mL) and a trace of sodium metal (0.005 g) at 130 °C for 30 min. The diethyl carbonate was then distilled off slowly over a period of 30 min. The residue was then distilled under vacuum at 128 °C (2 mm Hg): yield, 2.8 g (79.5%); IR (thin film) 1800 cm^{-1} (>C=O); ^1H NMR (60 M Hz) δ 3.37 (s, OCH_3), 3.67 (m, OCH_2), 4.77 (m, OCH).

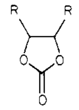
Butadiene Diepoxide (Racemic) (XI). *cis*-Butene-1,4-diol (IX), was converted to *rac*-2,3-dibromo-1,4-butanediol (X) which was cyclized to *rac*-butadiene diepoxide (XI) according to the literature procedure.[18]

1,4-Dimethoxy-2,3-butanediol (Racemic) (XII). *rac*-Butadiene diepoxide (25.8 g, 0.3 mol) was heated under reflux with 200 mL of methanol and 2 drops of 70% perchloric acid for 2 h. The reaction mixture was then neutralized with potassium hydroxide and concentrated under reduced pressure. XII was isolated by distillation under vacuum: bp 120 °C (12 mm); yield, 35.8 g (80%).

***trans*-4,5-Bis(methoxymethyl)-1,3-dioxolan-2-one (*trans*-IVa).** Transesterification of XII with diethyl carbonate was carried out as described for *cis*-IVa: mp 78 °C; yield, 70%; IR (thin film of $CHCl_3$solution) >C=O at 1798 cm^{-1}; ^1H NMR (60 M Hz) δ 4.65 (CH), 3.6 (CH_2, both multiplets ABC pattern), 3.42 (s, CH_3).

Methods. Inherent viscosities of poly(vinylene carbonate) were determined in Me_2SO and those of poly(hydroxymethylene) in 95% hydrazine. Employing solutions of 15% polymer concentrations, proton-noise-decoupled ^{13}C NMR spectra were recorded in the pulsed Fourier transform mode on either a Varian CFT-20 (20 MHz) or a Bruker HX270 (68 MHz) spectrometer. Solutions in Me_2SO-d_6 were used to obtain the spectra for poly(vinylene carbonate), poly(phenylvinylene carbonate), and poly(phenylvinylene glycol) with the solvent as the lock. Poly(hydroxymethylene) was studied in 90% N_2H_4 + D_2O, saturated solution of LiCl in D_2O, and saturated solution of LiCl in Me_2SO-d_6 respectively using D_2O or Me_2SO-d_6 as the lock. For the 20-MHz spectra a spectral width of 4000 Hz, an aquisition time of 0.45 s, and a pulse width of 6 to 10 μs were generally used. The noise band width was 1000 kHz, the number of data points was 4096, and the cumulative transients were in excess of 100 000. Pertinent peaks were then expanded digitally. The 68-MHz spectra were similarly recorded using a spectral width of 15 000 Hz. The individual peaks were expanded by a factor of 10. The peak areas were measured, where possible, using a DuPont 301 curve analyzer.

Table I
^{13}C NMR Chemical Shifts of 4,5-Disubstituted 1,3-Dioxolan-2-ones



	^{13}C NMR chemical shift (relative to Me_4Si, ppm) δ_R	δ_{CH}	$\delta_{C=O}$
IVa, R = CH_2OCH_3			
cis	69.66 (CH_2); 59.25 (CH_3)	77.16	154.52
trans	71.59 (CH_2); 59.39 (CH_3)	77.10	154.86
b, R = CH_3			
cis	14.27	76.4	154.82
trans	18.14	80.18	154.62
c, R = phenyl			
cis	133.7 (1′); 128.99 (2′); 128 (3′); 126.14 (4′)	81.26	154.72
trans	134.24 (1′); 129.76 (2′); 128.33 (3′); 127.33 (4′)	84.39	153.73

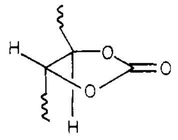
Table II
Effect of Polymerization Temperature on the Probability of cis Propagation in the Free-Radical Polymerization of Vinylene Carbonate

temp, °C	initiator	$P_{cis(m)}$[e]
3.0	γ ray (^{60}Co)[a]	0.3
35.0	DSBPD[b]	0.38
40.0	DSBPD[b]	0.32
60.0	AIBN[c]	0.36
100.0	$(t\text{-BuO})_2$[d]	0.36
135.0	$(t\text{-BuO})_2$[d]	0.35
160.0	$(t\text{-BuO})_2$[d]	0.34

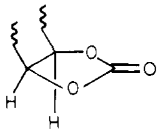
[a] Solid state; low conversion. [b] DSBPD: Di-*sec*-butyl peroxydicarbonate. [c] AIBN: 2,2′-azobis(isobutylronitrile). [d] $(t\text{-BuO})_2$: Di-*tert*-butyl peroxide. [e] $P_{cis(m)}$ determined from the ^{13}C NMR ratio of upfield to downfield carbonyl peaks (P_{cis} + P_{trans} = 1).

Results and Discussion

^{13}C NMR Studies on Poly(vinylene carbonate). Figure 1 shows the ^{13}C NMR spectrum of a typical poly(vinylene carbonate) sample prepared by free-radical initiation. The signal for the backbone carbons appears as a poorly resolved peak at δ 75. It does not reveal any configurational information; this is possibly due to the rather rigid nature of the chain in which the repeat unit is an inflexible cyclic carbonate ring system. However, two distinct peaks related to the carbonyl carbon atom appear that are about 0.3 ppm apart with a relative ratio of the downfield to the upfield peak of about 2:1 (Table II). The downfield carbonyl has been assigned to the trans monomer units (racemic, *r* or threo) and the upfield peak to the cis monomer units (meso, *m* or erythro).



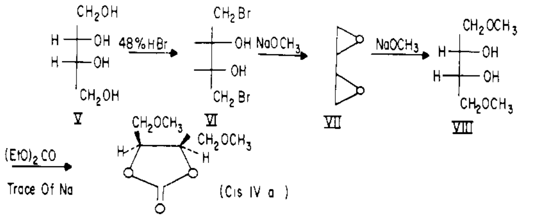
trans (*r*)



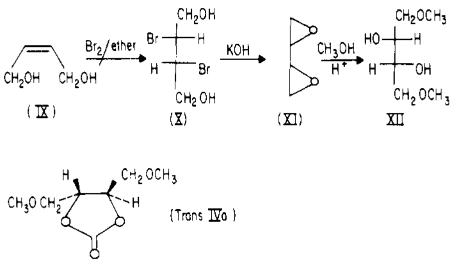
cis (*m*)

This assignment was confirmed by a study of ^{13}C NMR chemical shifts of typical model compounds, viz., 4,5-di-

Scheme I
Synthesis of *cis*-4,5-Bis(methoxymethyl)-1,3-dioxolan-2-one



Scheme II
Synthesis of *trans*-4,5-Bis(methoxymethyl)-1,3-dioxolan-2-one



substituted 1,3-dioxolan-2-ones (cis and trans) (Table II, IVa). *cis*- and *trans*-4,5-bis(methoxymethyl)-1,3-dioxolan-2-one are close analogues of poly(vinylene carbonate) since the substituents each carry an oxygen. Both of these compounds are unreported in the literature. The *cis*-4,5-bis(methoxymethyl)-1,3-dioxolan-2-one (*cis*-IVa) was synthesized from erythritol (V) according to the reaction Scheme I. Selective bromination of erythritol with 48% HBr gave *meso*-1,4-dibromo-2,3-butanediol (VI) which upon treatment with excess sodium methoxide in methanol led to *meso*-1,4-dimethoxy-2,3-butanediol (VIII) via the intermediate *meso*-1,3-butadiene diepoxide (VII). Transesterification of VIII with diethyl carbonate yielded *cis*-IVa. The trans isomer (*trans*-IVa) was synthesized from *cis*-butene-1,4-diol (IX) according to reaction Scheme II. The reaction entailed bromination of IX to *rac*-2,3-dibromobutane-1,4-diol (X), cyclization to *rac*-1,3-butadiene diepoxide (XI), subsequent methanolysis to yield 1,4-dimethoxy-2,3-butanediol (*rac*-XII), and finally transesterification with diethyl carbonate.

In the ^{13}C NMR of *cis*- and *trans*-IVa, the trans isomer indeed showed the carbonyl resonance at about 0.34 ppm downfield from that of the cis isomer. It may by noted however that the chemical shift of the carbonyl carbon is sensitive to the stereochemistry and the nature of the substituent. Substitution with a phenyl group in the cyclic carbonate (IVc) resulted in a reversal of the chemical shifts, the cis carbonyl being downfield from that of the trans isomer. The unusual steric constraint in the *cis*-4,5-diphenyl-1,3-dioxolan-2-one forces the phenyl rings to be positioned face to face; hence the carbonyl carbon experiences less shielding from the π-electron cloud.

The approximate 2:1 trans/cis ratio found in poly(vinylene carbonate) prepared by free-radical initiation was essentially independent of the temperature of polymerization (Table II) in the temperature range of 3 to 160 °C. Thus the probability of cis propagation $P_m = \sigma = 0.35 \pm 0.05$ and that of trans propagation $P_r = 1 - \sigma = 0.65 \pm 0.05$. Substitution in the Arrhemius rate equation yields according to

$$P_m/P_r = \exp\{[(\Delta S^{\ddagger}_m - \Delta S^{\ddagger}_r)/R] - (\Delta H^{\ddagger}_m - \Delta H_r)/RT\}$$

a value of $\Delta\Delta H_p = 0$ and $\Delta\Delta S = 1.4$ eu. This indicates that the 2:1 preference of trans propagation is favored by entropy factors. Thus whereas the primary observable units in poly(vinylene carbonate) are cis (*m*) and trans (*r*) monomer units, further information concerning the stereochemistry of the polymer could be obtained only from the study of its hydrolysis product, viz., poly(hydroxymethylene) (PHM).

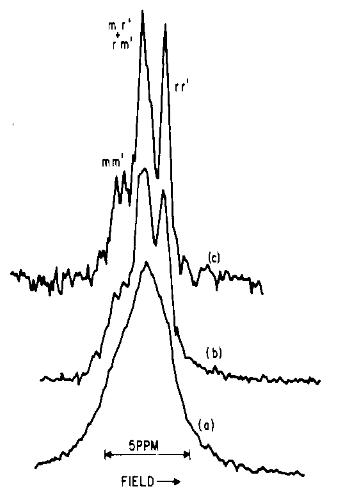


Figure 2. ^{13}C NMR (20 MHz) of poly(hydroxymethylene) in saturated aqueous LiCl at: (A) 60 °C; (B) 100 °C; (C) 140 °C.

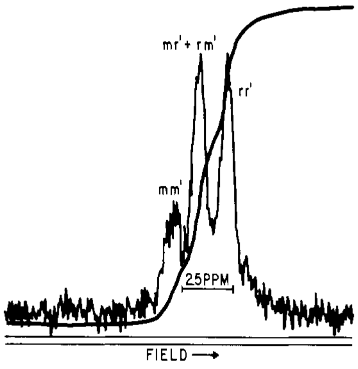


Figure 3. ^{13}C NMR of poly(hydroxymethylene) in saturated LiCl in Me_2SO-d_6 at 140 °C (20 MHz).

Configuration Statistics and Stereochemistry of Poly(vinylene carbonate) and PHM. During polymerization of vinylene carbonate, addition of monomer to the propagating radical generates both cis (*m*) and trans (*r*) monomer units in the chain with respective probabilities of $P_m = \sigma$ and $P_r = 1 - \sigma$. However, each pair of monomer units may be linked via meso (*m'*, anti) or racemic (*r'*, syn) junction bonds for which another probability parameter may be introduced as $P_{m'} = \alpha$ and $P_{r'} = 1 - \alpha$.

Although the two configurational units (*m'* and *r'*) are different for poly(vinylene carbonate) they are indistinguishable after hydrolysis to PHM. The configuration probabilities for poly(vinylene carbonate) and PHM are shown in Tables III and IV.

^{13}C NMR of Poly(hydroxymethylene). PHM prepared by hydrazinolysis or alkaline hydrolysis retains the configurational structure of the corresponding poly(vinylene carbonate). Since the reaction involves only the carbonyl group it is suitable for structural studies. Prior to our study there was no known solvent for high molecular weight PHM and the polymer was known to be intractable and insoluble in most common solvents, a property undoubtedly attributable to the strong intra- and intermolecular hydrogen bonding. We found several new solvent systems for this polymer. The most notable among these were anhydrous (>95%) hydrazine and saturated solutions of LiCl in either water or Me_2SO, all of which possess powerful hydrogen bonding capabilities. ^{13}C

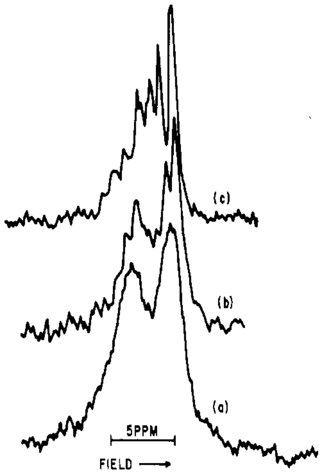


Figure 4. ^{13}C NMR (20 MHz) of poly(hydroxymethylene) in 90% hydrazine + 10% D_2O at: (A) 25 °C; (B) 60 °C; (C) 100 °C (methine resonance expanded).

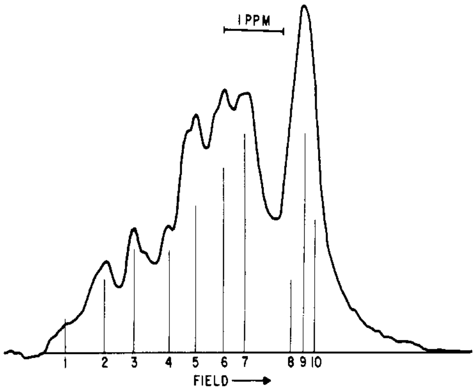
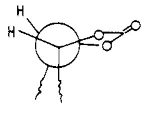
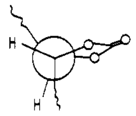
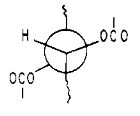
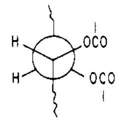
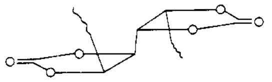
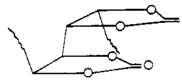
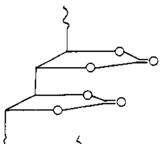
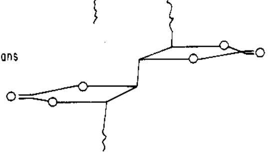
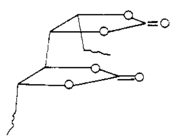
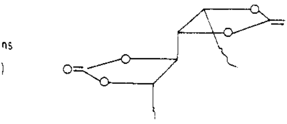


Figure 5. High-resolution ^{13}C NMR (68 MHz) of poly(hydroxymethylene) in 90% N_2H_4 + 10% D_2O at 100 °C (methine resonance expanded); vertical lines represent calculated pentad probabilities (Table V).

(proton decoupled) NMR spectra recorded in these solvents at various temperatures are shown in Figures 2 to 5. In PHM, there is only one chemically distinct carbon, viz., CHOH which appears at ~75 ppm. However since each carbon in the chain is pseudoassymmetric, resolution due to configurational differences is possible.

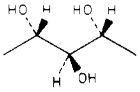
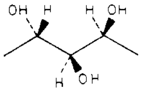
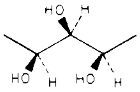
From among the possible different configurational sequences in PHM there are three observable triads and ten pentads; they are shown in Table IV. The notations *m′* and *r′* used for the junction bonds in poly(vinylene carbonate) are retained for the purpose of probability calculation although they are indistinguishable from *m* and *r*. The spectral resolution of PHM is significantly influenced by the temperature and the nature of the solvent employed. This is due to conformational changes involving solvent–polymer and polymer–polymer hydrogen bonding effects. In saturated aqueous LiCl (Figure 2), the unresolved single peak, observed below 60 °C, begins to resolve at 100 °C. The line broadening is not only due to the macroscopic viscosity but also due to the microscopic viscosity, i.e., the rigid conformation of the polymer. Above 100 °C three major peaks are observed in the approximate ratio of 1:2.5:1.5, although the downfield peak shows a distinct substructure. The spectrum in saturated solutions of LiCl in Me_2SO-d_6 (Figure 3) at 140 °C is similar to that in aqueous LiCl. These three peaks may be assigned to *mm′*, *mr′* + *rm′*, and *rr′* triads in the order of the increasing field. These primary configurational sequences of PHM must be in the ratio of 0.175:0.5:0.325 (Table IV), based on the observed value $\sigma = 0.35$ and for a value of $\alpha = 0.5$, i.e., random syn and anti placement of monomer units in the precursor poly(vinylene carbonate). As the discrimination increases, resolution of the pentads should, in principle, be possible.

Table III
Configuration Units in Poly(vinylene carbonate)

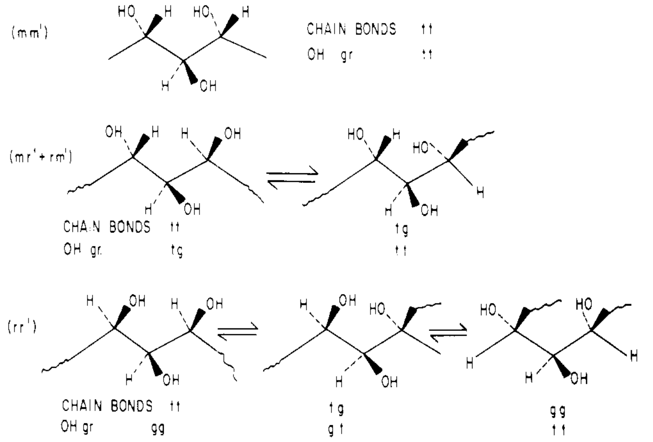
Dyads		Bernoullian Probability
Cis monomer unit (m)		σ
Trans monomer unit (r)		$1-\sigma$
Anti junction bond (meso, m′)		α
Syn junction bond (rac, r′)		$1-\alpha$
Tetrads		
Cis-anti-cis mm′m		$\sigma^2\alpha$
Cis-Syn-cis mr′m		$\sigma^2(1-\alpha)$
Trans-syn-Trans rr′r		$(1-\sigma)^2(1-\alpha)$
Trans-anti-trans rm′r		$(1-\sigma)^2\alpha$
Cis-syn-Trans (mr′r + rr′m)		$2\sigma(1-\sigma)(1-\alpha)$
Cis-anti-Trans (mm′r + rm′m)		$2\sigma(1-\sigma)\alpha$

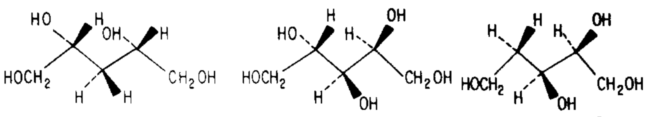
The spectra in hydrazine, a better solvent for PHM, provided this information. At 25 °C in hydrazine, however, two peaks of about equal intensity appeared, possibly due to partial overlap of *mr′* + *r′m* triad having two conformer populations with chemical shifts close to *mm′* and *rr′*. At higher temperature, the spectral resolution was greatly improved showing the pentad sequences at 100 °C, the tentative assignment of which is shown in Figure 5. The rationale for these assignments is as follows: For the three triads *mm′*, *mr′* + *rm′*, and *rr′* highest solvation, i.e., stabilization by polymer solvent hydrogen bonding, occurs

Table IV
Configurational Sequences in Poly(hydroxymethylene)

	bernoullian probability (P)			
		P at σ = 0.35 and		
sequence	P	$\alpha = 0$	$\alpha = 0.5$	$\alpha = 1.0$
	Triads			
1. *mm'* 	$\sigma\alpha$	0	0.175	0.35
2. *mr'* + *rm'* 	$\sigma(1-\alpha) + \alpha(1-\sigma)$	0.35	0.5	0.65
3. *rr'* 	$\sigma\alpha$	0.65	0.325	0
	Pentads			
mm centered				
1. *mm'mm'*	$\sigma^2\alpha^2$	0	0.030625	0.1225
2. *rm'mr*	$\sigma(1-\sigma)\alpha(1-\alpha)$	0	0.056875	0
3. *rm'mm'* + *mm'mr'*	$\sigma(1-\sigma)\alpha^2 + \sigma^2\alpha(1-\alpha)$	0	0.0875	0.2275
mr centered				
4. *mm'rm'* + *mr'mm'*	$\sigma(1-\sigma)\alpha^2 + \sigma^2\alpha(1-\alpha)$	0	0.0875	0.2275
5. *mm'rr'* + *rr'mm'*	$2\sigma(1-\sigma)\alpha(1-\alpha)$	0	0.11375	0
6. *rm'rm'* + *mr'mr'*	$(1-\sigma)^2\alpha^2 + \sigma^2(1-\alpha)^2$	0.1225	0.13625	0.4225
7. *rm'rr'* + *rr'mr'*	$(1-\sigma)^2\alpha(1-\alpha) + \sigma(1-\sigma)(1-\alpha)^2$	0.2275	0.1625	0
rr centered				
8. *mr'rm'*	$\sigma(1-\sigma)\alpha(1-\alpha)$	0	0.056875	0
9. *rr'rm'* + *mr'rr'*	$(1-\sigma)^2\alpha(1-\alpha) + \sigma(1-\sigma)(1-\alpha)^2$	0.2275	0.1625	0
10. *rr'rr'*	$(1-\sigma)^2(1-\alpha)^2$	0.4225	0.105625	0

when the OH groups are disposed in trans conformation to each other. This is based on the analogy of observed conformer populations for meso and racemic 2,4-pentanediols in water and polar solvents.[16] Thus solvation of OH groups forces the local conformation of *mr'* and *rr'* units to a helical state with chain bonds in gauche position. Since the shielding effects in ^{13}C NMR are generally due to gauche carbon–carbon interactions, the chemical shifts will be progressively upfield as we go from *mm*, *mr'*, to *rr'*:





D-RIBITOL(mm) $\delta C_3^* = 118.4$, D-ARABITOL(mr) $\delta C_3^* = 120$, D-XYLITOL(rr) $\delta C_3^* = 120.1$
(*PPM rel to CS_2)

This hypothesis is further confirmed by the observed chemical shifts[17] of the carbon 3 in pentitols, the model compounds for the triads, which appears progressively upfield as we go from ribitols (*mm*) and arabitol (*mr*) to xylitol (*rr*).

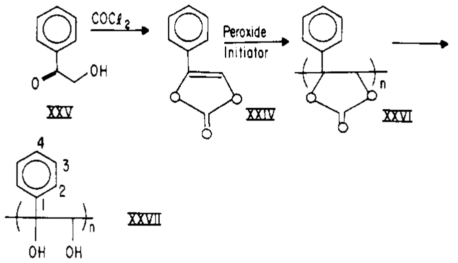
Extending the arguments presented above to pentad sequences (Table IV), it may easily be seen that the three *rr* centered pentads *rr'rr*, *rr'rm'* + *mr'rr'*, and *mr'rm'* are expected to have rigid local helical conformations and hence must be the most upfield and least resolved ones. The three lines actually appear to overlap to form a large upfield peak accounting for 30% of the total spectral area (Figure 3). The calculated pentad probabilities (for σ = 0.35, α = 0.5) shown in Table IV appear to agree well with the observed spectrum (Figure 3). Thus the sum of probabilities of pentads 8 to 10 is equal to 0.326. The rest of the pentads (no. 1 to 7) are well resolved and are assigned in the order of decreasing field strength (Figure 3), although some of the downfield peaks tend to show even further substructures. While an NMR study of isomeric heptitols may provide further proof, this work has shown that poly(hydroxymethylene), derived from the free-radical polymerization of vinylene carbonate, is essentially atactic with a slight preponderance of racemic diol units as indicated by:

$$P_{rac\text{-}diol}(r \equiv r') = \tfrac{1}{2}(P_r + P_{r'}) \simeq 0.575$$

Thus the low stereoselectivity of free-radical propagation normally observed with most vinyl monomers also holds true for the polymerization of vinylene carbonate.

Poly(phenylvinylene carbonate) and Poly(phenylvinylene glycol). ^{1}H and ^{13}C NMR Study of Microtacticity. Phenyl(vinylene carbonate) prepared by condensation of phenacyl alcohol (XIII) with phosgene may be polymerized to poly(phenylvinylene carbonate) (XV) by free-radical initiation (Scheme III). The po-

Scheme III
Synthesis of Poly(phenylvinylene glycol)



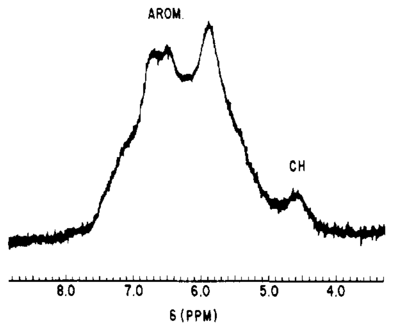
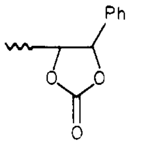


Figure 6. ^{1}H (100 MHz) NMR of poly(phenylvinylene carbonate) in Me$_2$SO-d_6 at 150 °C.

lymerization of the monomer is particularly interesting in view of the expected steric crowding in the chain due to the phenyl and carbonate rings. Since the monomer is structurally close to vinylene carbonate, the stereochemistry of propagation is expected to be similar, though with some notable differences. The propagating radical would be the phenyl-substituted carbon due to the resonance stabilization of the radical by the phenyl group as it is known for styrene. The addition of each monomer unit generates threo (*t*, trans) and erythro (*e*, cis) monomer units in the chain, which may be linked via threo (*t*′, syn) or erythro (*e*′, anti) junction bonds (Table V). Unlike in poly(vinylene carbonate), the linking of a threo unit to either a threo or erythro unit causes unfavorable phenyl–phenyl interactions (tetrads *tt′t*, *te′t*, *et′t*, and *ee′t* Table V), whereas the erythro units have the usual gauche carbon–carbon interaction (nearly eclipsed, dihedral angle ≤20 °C). Hence to a first approximation all units have nearly the same energy with perhaps the erythro units being more favored. Hydrolysis (or hydrazinolysis) of poly(phenylvinylene carbonate) yields poly(phenylvinylene glycol) (XVI), a polymer not described in the literature. Interestingly, this polymer is soluble in Me$_2$SO, unlike PHM which is insoluble in all common solvents. Obviously the hydrogen bonding in XVI is less efficient due to the bulkiness of the phenyl groups. For configurational studies by NMR the methine proton in poly(phenylvinylene glycol) is uniquely suited since there is no vicinal proton causing spin–spin coupling. ^{1}H NMR (100 MHz) of poly(phenylvinylene carbonate) in Me$_2$SO-d_6 shows rather broad and poorly resolved aromatic and methine peaks (Figure 6) undoubtedly due to the very rigid nature of the backbone causing line broadening even at 150 °C. Hydrolysis of the cyclic carbonate units to diol units is expected to increase the segmental mobility. Indeed, in poly(phenylvinylene glycol) the methine proton resolves into three distinct, partially overlapping peaks (Figure 7). The peaks may be assigned to the three primary configurational sequences, viz., triads *e′e*, *e′t* + *t′e*, and *t′t* in the order of increasing field strength (Table VI). For a completely atactic polymer ($\sigma = 0.5$, $\alpha = 0.5$), the three peaks must be in the ratio of 0.25:0.5:0.25 assuming Bernoullian probability (Table VI). The observed ratio of 0.3:0.5:0.2 is in agreement with an atactic structure of the polymer with perhaps a slight preference for erythro propagation. It is interesting, however, to note that threo propagation does indeed occur in spite of the expected phenyl–phenyl interaction indicating that the propagation is a kinetically controlled process which is characteristic of a free-radical mechanism.



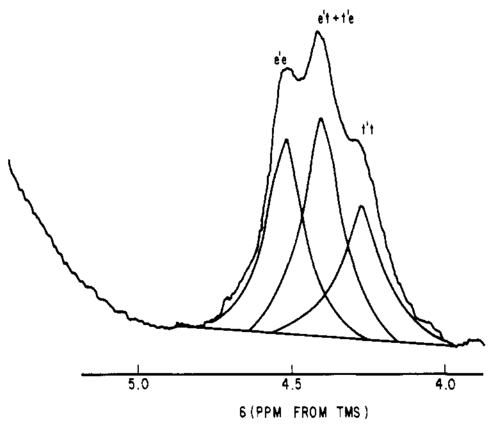


Figure 7. ^{1}H (270 MHz) NMR of poly(phenylvinylene glycol) in Me$_2$SO-d_6 at 100 °C.

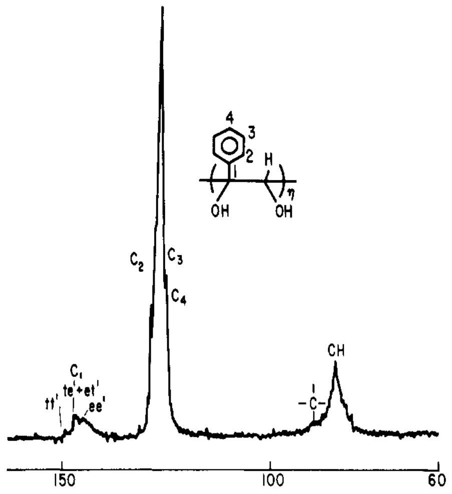


Figure 8. ^{13}C NMR (20 MHz) of poly(phenylvinylene glycol) in Me$_2$SO-d_6, 140 °C.

Proton-decoupled ^{13}C NMR of poly(phenylvinylene glycol) in Me$_2$SO-d_6 at 140 °C indicate little resolution of the backbone carbons (>C< and CH) as well as the C$_2$, C$_3$, C$_4$ carbon atoms of the phenyl ring. The C$_1$ carbon of the phenyl ring in XVI, appearing most downfield, indicates resolution into the three triads *tt′*, *te′* + *et′*, and *ee′* (Figure 8 and Table VI).

Inoue et al.[18] found that in the ^{13}C NMR of polystyrene the C$_1$ resonance of the phenyl ring is sensitive to configuration and provides even pentad resolution in contrast to the C$_2$, C$_3$, and C$_4$ for which no configurational resolution was indicated.

^{13}C NMR of poly(phenylvinylene glycol) in hydrazine (Figure 9) at 100 °C, interestingly, shows resolution of the C$_2$, C$_3$, and C$_4$ carbons of the phenyl ring. Each of these carbons must in principle give rise to three triads (1b, 2b,

Table V
Configuration Units in Poly(phenylvinylene carbonate)

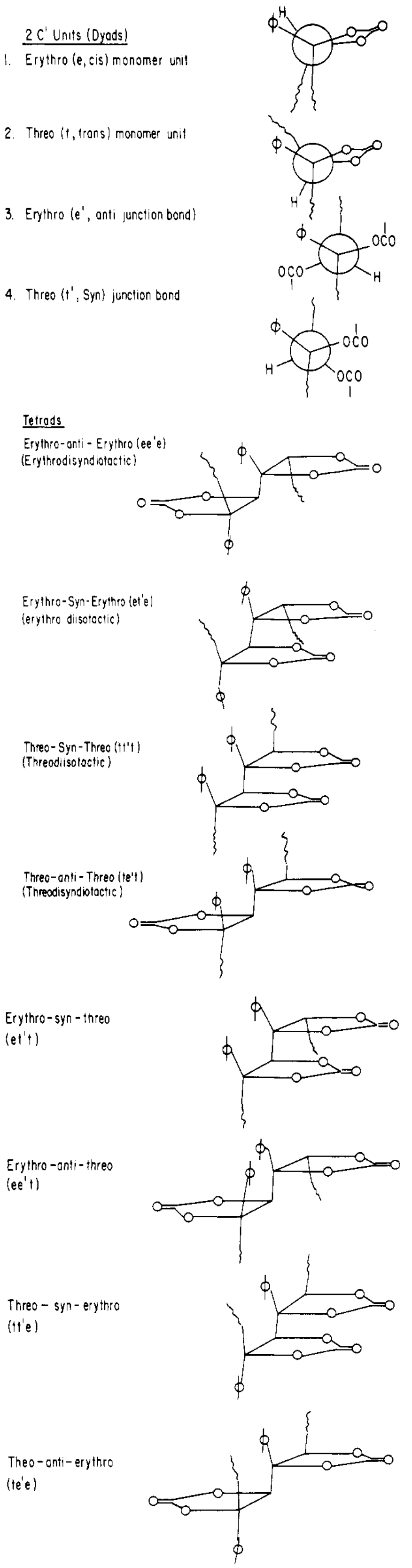
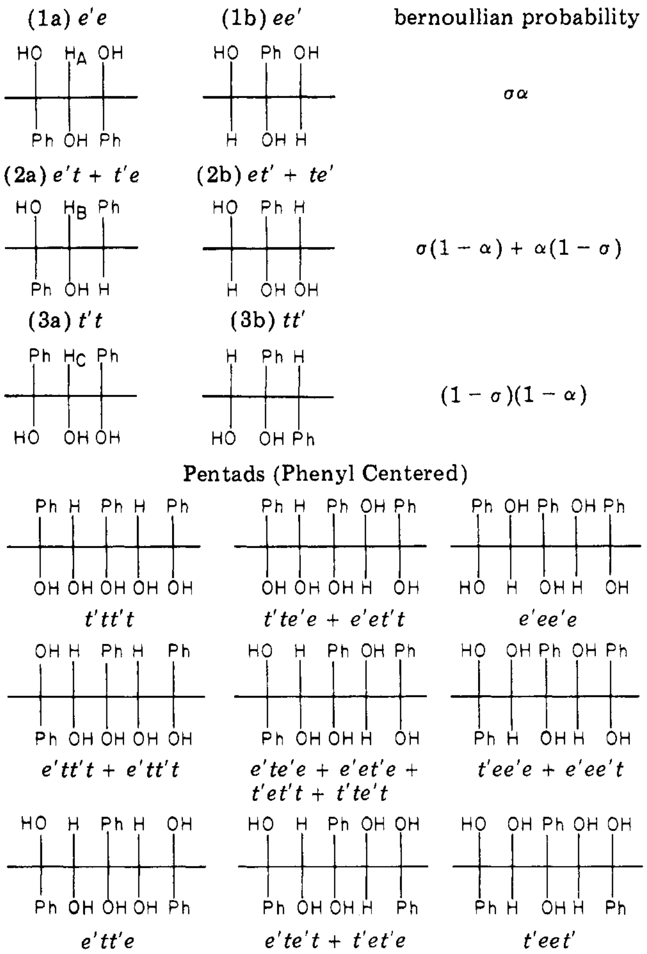


Table VI
Configurational Sequences in Poly(phenylvinylene glycol)[a]



[a] In poly(phenylvinylene glycol) *t* and *e* are indistinguishable from *t'* and *e'*.

and 3b in Table VI) or nine possible pentads, i.e., a total of 9 lines for triads or 27 lines for pentads. The observed spectrum indicates some pentad resolution (about 20 lines). However, partial overlap of these pentads makes the assignment of the peaks rather difficult. In summary, the ^1H NMR of the methine proton and ^{13}C NMR of C_1 carbon in the poly(phenylvinylene glycol) confirm the atactic structure of the polymer with both threo and erythro diol units in the chain.

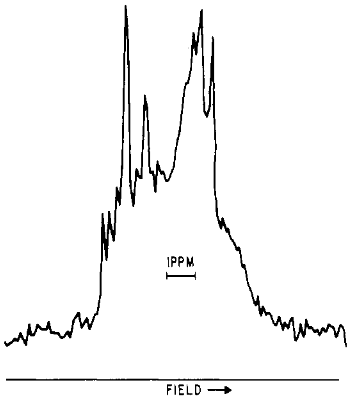


Figure 9. ^{13}C NMR (20 MHz) of poly(phenylvinylene glycol) in 90% N_2H_4 + 10% D_2O at 140 °C (aromatic region C_2, C_3, and C_4 expanded).

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Sequential Analysis by Cooperative Reactions on Copolymers. 4. The Structure of Locust Bean Gum and Guaran

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ABSTRACT: Galactomannans like locust bean gum and guaran consist of a backbone of mannose units some of which have galactose side stubs. On reaction of these galactomannans with periodate both galactose and mannose units get oxidized. We show how to correct for the consumption of periodate by the galactose units. After this step the periodate oxidation of the mannan backbone and the methylation analysis of the galactomannan can be described by the theory developed by P. C. Hemmer and the author for reactions on stationary second-order Markovian copolymers. This provides the approximate sequential structure of guaran and locust bean gum.

I. Introduction

In this paper we apply the theory developed recently[1-4] to describe the periodate oxidation[5,6,8] and the methylation analysis[6,7] of the two important galactomannans locust bean gum and guaran.

For convenience of the reader we give a brief survey of the assumptions made and of the results obtained in our previous work.[1-4]

We consider very long linear polymers consisting of two different monomeric units $i = 1, 2$. The chains are assumed to be stationary second-order Markov chains: p_{ijl} is the conditional probability that a given unit is of type l given that the two preceding ones are of type i and j. In a very long copolymer most of the units will conform to stationarity, i.e., end effects will be negligible in the limit of an infinitely long polymer.

Introducing p_j as the probability that an arbitrary unit is of type j and p_{ij} as the conditional probability that a unit is of type j given that it is preceded by an i unit, these probabilities are completely determined in terms of the second-order Markovian probabilities p_{ijl}:[2-4]

$$p_{11} = p_{211}/(p_{112} + p_{211}) \tag{1}$$

$$p_{12} = p_{112}/(p_{112} + p_{211}) \tag{2}$$

$$p_{21} = p_{221}/(p_{122} + p_{221}) \tag{3}$$

$$p_{22} = p_{122}/(p_{122} + p_{221}) \tag{4}$$

and

$$p_1 = p_{21}/(p_{12} + p_{21}) \tag{5}$$

$$p_2 = p_{12}/(p_{12} + p_{21}) \tag{6}$$

The reaction process is assumed to obey the following rules: The probability that an arbitrarily placed unit of type j reacts in the time interval dt is equal to zero if the unit has already reacted, otherwise equal to k_j dt if its two adjacent units are unreacted, equal to $a_l^j k_j$ dt if out of its neighbors only the right one has reacted and is of type l, equal to $\tilde{a}_i^j/k_j$ dt if out of its neighbors only the left one has reacted and is of type i, and equal to $c_i{}^j{}_l k_j$ dt if it is between two reacted species, from left to right i,l.

The extent of reaction $y_j(t)$ of unit type $j = 1, 2$ at time t in an infinitely long polymer chain is given by:[3,4]

$$\begin{aligned} y_j(t) = p_j - p_j \sum_{i=1}^{2}\sum_{l=1}^{2} p_{ji}p_{ijl}e^{-k_jc_i{}^j{}_lt} + \\ k_jp_j\sum_{i=1}^{2}\sum_{l=1}^{2} p_{ji}p_{ijl}e^{-k_jc_i{}^j{}_lt}\Big\{(1 - a_i^j - \tilde{a}_i^j + \\ c_i{}^j{}_l)\int_0^t \mathrm{d}s\ e^{k_j(c_i{}^j{}_l-1)s}\pi_{jl}(s)\tilde{\pi}_{ji}(s) + \\ (a_l^j - c_i{}^j{}_l)\int_0^t \mathrm{d}s\ e^{k_jc_i{}^j{}_ls}\nu_{jl}(s)\tilde{\pi}_{ji}(s) + \\ (\tilde{a}_i^j - c_i{}^j{}_l)\int_0^t \mathrm{d}s\ e^{k_jc_i{}^j{}_ls}\pi_{jl}(s)\tilde{\nu}_{ji}(s)\Big\} \end{aligned} \tag{7}$$

The quantities $\nu_{jl}(s)$, $\pi_{jl}(s)$, $\tilde{\nu}_{jl}(s)$, and $\tilde{\pi}_{jl}(s)$ entering eq 7 are probabilities referring to the state of reaction of the first two units in an infinitely long polymer chain[3,4] at time $s = -\ln \zeta$. They are given by

$$\nu_{jl}(\zeta) = \zeta^{k_ja_l^j} \sum_{n,p=1}^{2} \sum_{t,v=1}^{2} \Phi_{jl;np}(\zeta)\Phi^{-1}{}_{np;tv}(1) \tag{8}$$

$$\pi_{jl}(\zeta) = \sum_{r=1}^{2} p_{jlr}\nu_{lr}(\zeta) \tag{9}$$

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