

The Microstructure of Poly(divinyl acetal)s as Determined by ^{13}C NMR Spectroscopy. Ring Stereochemistry and Isomerization Propagation*

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ABSTRACT: Divinyl formal, acetaldehyde divinyl acetal, and acetone divinyl acetal were polymerized freeradically, and the polymer structures were determined by detailed analyses of ^{13}C NMR spectra. The carbon chemical shifts of various structures which might be formed by simple propagation, by cyclopolymerization, and by isomerization propagation were derived from those of a variety of model compounds and their combinations. All the polymers contained the *cis*-4,5-disubstituted-1,3-dioxolane ring as the predominant structural unit in the main chain (*ca.* 75%) and as the pendent group (*ca.* 25%). The latter structure was formed by hydrogen abstraction of the propagating methylenedioxolane radical from the neighboring methylene group. Similar hydrogen migration conceivably occurred also during the polymerization of diallylamines.

KEY WORDS ^{13}C NMR Spectroscopy / Poly(divinyl formal) / Poly(divinyl acetal) / Cyclopolymerization / Steric Structure /

Divinyl formal and divinyl acetals readily undergo radical cyclopolymerization.¹⁻⁸ These polymers are partially cyclized and the cyclized structure may be composed of five- and/or six-membered rings (see Scheme 1).^{3,4} In addition, the formation of the isomerized and other structural units was reported in several cases.⁵⁻⁷ The polymer structure could be inferred also from the oligomer structure.⁹ These structure determinations have been performed by chemical means (hydrolysis and the subsequent determination of the 1,2-glycol content), and by IR and ^1H NMR spectroscopies. However, the conclusions were not necessarily definitive, and the stereochemical information was totally nonexistent.

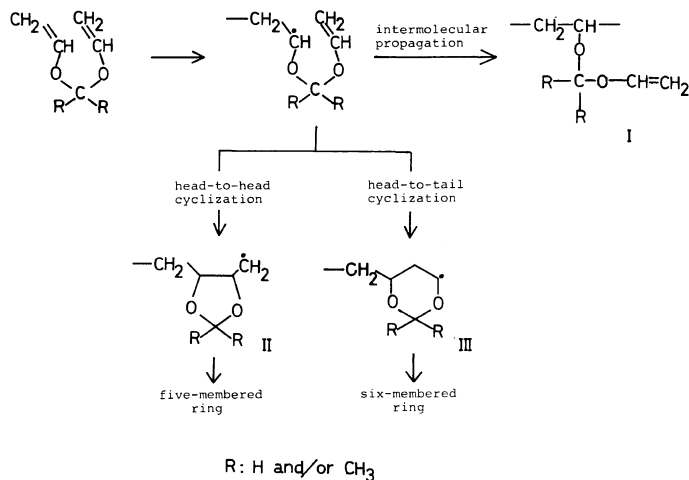
Recently, it was shown that ^{13}C NMR spectroscopy was a very powerful tool for elucidation of the microstructure of several cyclopolymers.^{10,11} Therefore, we carried out a detailed investigation of the ^{13}C NMR spectrum of poly(divinyl formal) and poly(divinyl acetal)s.

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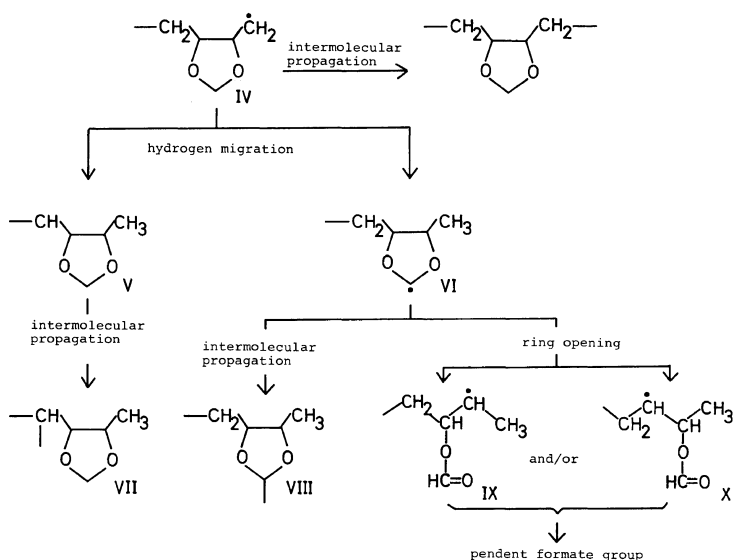
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The modes of propagation of divinyl formal and divinyl acetals which have been described in the literature are summarized in Schemes 1, 2, and 3. These monomers will propagate *via* the uncyclized (I) and cyclized radicals (Scheme 1). The cyclized radical may be five-membered (II) and/or six-membered (III), and may undergo rearrangements. Probable radical rearrangement processes for the five-membered radical (as formed by the head-to-head cyclization) are shown in Scheme 2 in the case of divinyl formal. The hydrogen abstraction from the formal methylene group accompanied by ring opening gives rise to the formate pendent group (VI→IX and/or X). Simple propagation may occur from the formal carbon in the absence of ring opening (VI→VIII). On the other hand, hydrogen abstraction from the adjacent methylene group will yield a pendent dioxolane ring (V→VII). Similar processes are conceivable for the six-membered radical, as described in Scheme 3.

The same situation should arise for the other monomers, except that hydrogen migration from the acetal carbon is not possible for acetone divinyl acetal.



Scheme 1



Scheme 2

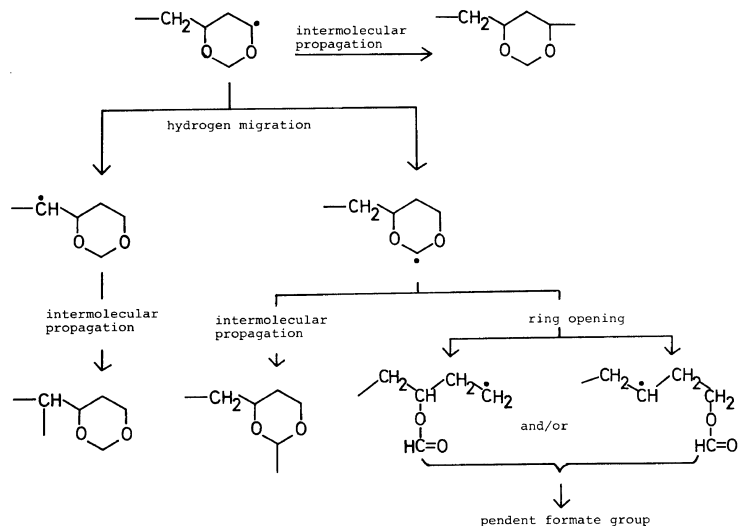
EXPERIMENTAL

Materials

Divinyl formal (DVF) was prepared according to the literature³ by dehydrochlorination of β , β' -dichloroethyl formal (bp 103–105°C/24 mmHg), which in turn was obtained from paraformaldehyde and ethylene chlorohydrin. The crude product was washed with aqueous sodium bisulfite and water, dried over KOH, and distilled from CaH₂: bp

89–91°C, $n_D^{20} = 1.4155$ (lit.³ bp 89–90°C, $n_D^{23} = 1.4143$). Acetaldehyde divinyl acetal (CH₃-DVA) was similarly prepared by dehydrochlorination over KOH from acetaldehyde dichloroethyl acetal (bp 90–92.5°C/10 mmHg, lit.¹² bp 100°C/9 mmHg), which was obtained from vinyl acetate and ethylene chlorohydrin. The work-up was the same as above: bp 103°C (lit.¹² 103°C). In the case of acetone divinyl acetal (2CH₃-DVA), acetone dichloroethyl acetal was prepared by the reaction of

Cyclopolymerization of Divinyl Acetals



Scheme 3

acetone dimethyl acetal and ethylene chlorohydrin: bp 72–75°C/3 mmHg (lit.¹³ bp 75°C/2 mmHg). This compound was dehydrochlorinated over KOH under slightly reduced pressure. The distillate was dried over MgSO₄ and fractionally distilled: bp 64.5–65.5°C/140 mmHg (lit.¹³ bp 53–55°C/95 mmHg). The structure and purity of these monomers were confirmed by IR and ¹H NMR spectroscopies and by gas chromatography.

1,3-Dioxolanes were prepared according to the procedures described in the literature^{14–16} and identified by IR and NMR spectroscopies and gas chromatography. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Solvents were purified by the conventional procedures.

Polymerization

Monomer, AIBN, and benzene (when necessary) were placed in ampoules, subjected to the freeze-pump-thaw cycle, and sealed under vacuum. Polymerizations were carried out by immersing the ampoule in a constant temperature bath. Poly(divinyl formal) prepared in benzene was precipitated by petroleum ether, reprecipitated from benzene and petroleum ether, and dried. *Anal.* Found: C, 60.18%; H, 8.01%; N, 0.24%. Calcd for C₅H₈O₂: C, 59.98%; H, 8.05%. The polymerization mixture (bulk) of acetaldehyde divinyl acetal was diluted with benzene and poured into methanol. The precipitate was dissolved in benzene and freeze-dried. *Anal.* Found: C, 63.57%; H, 8.78%; N, 0.13%. Calcd for

C₆H₁₀O₂: C, 63.14%; H, 8.83%. The polymerization mixture of acetone divinyl acetal was diluted with benzene and acetone, and poured into dry methanol. Reprecipitation was repeated and the precipitate was dried *in vacuo*. *Anal.* Found: C, 65.04%; H, 9.37%; N, 0.07%. Calcd for C₇H₁₂O₂: C, 65.60%; H, 9.44%. The polymerization results are summarized in Table I. Bulk divinyl formal polymerized violently under the present condition, to give a crosslinked product. The other polymers were white powders and soluble in benzene, CCl₄, and tetrahydrofuran.

Miscellaneous

¹³C NMR spectra were obtained using a 22.63-MHz Bruker FT-NMR instrument under noise decoupling. The samples were 40 wt% solutions in a mixture of benzene and benzene-*d*₆; pulse width, 7 μs; sweep width, 4000/60 Hz/cm; accumulation, 5,000–10,000 scans.

The molecular weights of the polymers were determined by a Hitachi gel-permeation chromatograph (Model 635). Three columns of different molecular weight ranges were connected in series, and tetrahydrofuran was used as eluent. The molecular weight was calculated based on a calibration curve of monodisperse polystyrenes.

RESULT AND DISCUSSION

Structure of Poly(divinyl formal)

The ¹³C NMR spectrum of poly(divinyl formal) is

shown in Figure 1. The spectrum is made of eleven peaks in the range of 15 to 95 ppm, and does not possess peaks which are assignable to the vinyl carbon (*ca.* 85 and 140–150 ppm)¹⁷ or to the carbonyl carbon of the formate group (*ca.* 161 ppm).¹⁸ Weak absorptions are, however, observed in the 1600–1670 cm⁻¹ region in the IR spectrum. They may be attributed to the pendent double bond (1640 cm⁻¹, broad) and the ester carbonyl group (1725 cm⁻¹).

The ¹H NMR data of this polymer sample was consistent with the ¹³C NMR data, in that peaks due to the vinyl and formate protons were not observed. The absence of the vinyl group is in agreement with the previous conclusions^{3,5} that the residual unsaturation is usually less than 5%. Aso, *et al.*,⁵ used IR and ¹H NMR spectroscopies to detect small amounts of the formate group. However, its presence could not be detected in the ¹³C NMR spectrum for

poly(divinyl formal) of Table I.

The use of appropriate model compounds is indispensable for the reliable assignment of the polymer ¹³C NMR data. The ¹³C NMR data of the following model compounds have been published: 1,3-dioxanes,¹⁹ formate, and acetates,¹⁸ branched alkanes,²⁰ cyclopentanes and cyclohexanes,²¹ and vinyl ethers.²² The ¹³C-NMR data of 1,3-dioxolanes were obtained by us and are summarized in Table II. Recently, Senda, *et al.*,²³ reported ¹³C NMR data for some of the compounds. The reported chemical shifts agreed with our own data within 0.5 ppm.

The carbon chemical shifts of the various structural units were calculated from those of the model compounds according to the procedure illustrated as an example in Scheme 4. The peak of the substituted ring carbon in *trans*-1,2-dialkylcyclopentane undergoes a downfield shift by 4.8 ppm by elongation of the alkyl substituent (methyl to ethyl). This shift

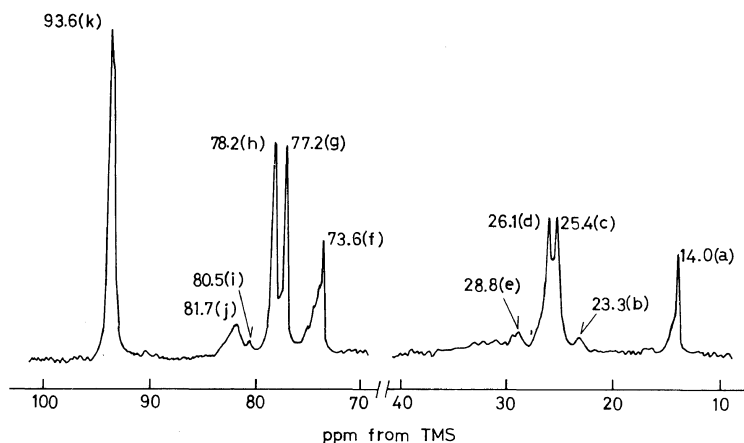


Figure 1. ¹³C-NMR spectrum of poly(divinyl formal). 40 wt% in C₆D₆/C₆H₆. Internal reference, benzene.

Table I. Radical polymerization of divinyl acetals

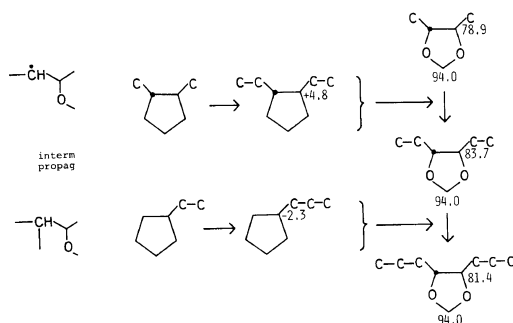
Monomer,	mol/l	AIBN, mol/l	Solvent	Polymeri- zation temp, °C	Polymeriza- tion time	Conver- sion, %	Molecular weight ^b		
							\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
DVF	2.6	1.8×10^{-2}	Benzene	70	20.5 h	36.2	7700	20500	2.68
DVF	9.1 ^a	9.1×10^{-2}	—	80	1–2 min	Gelation	—	—	—
CH ₃ -DVA	7.8 ^a	7.8×10^{-2}	—	80	25 min	27.6	17400	37300	2.15
2CH ₃ -DVA	6.8 ^a	7.0×10^{-2}	—	80	40 min	21.7	28800	37300	1.29

^a Bulk polymerization. ^b Estimated by gel-permeation chromatography.

Table II. Carbon-13 chemical shifts of methyl-substituted 1,3-dioxolanes^a

Substituents	C-2	C-4	C-5	CH ₃ (C-2)	CH ₃ (C-4)	CH ₃ (C-5)
<i>cis</i> -4,5-Me ₂	93.6	74.1	74.1	—	14.3	14.3
<i>trans</i> -4,5-Me ₂	94.0	78.9	78.9	—	16.6	16.6
2- <i>cis</i> -4, <i>cis</i> -5-Me ₃	100.7	74.5	74.5	20.6	15.1	15.1
2- <i>trans</i> -4, <i>trans</i> -5-Me ₃	99.6	74.0	74.0	21.0	13.8	13.8
2- <i>cis</i> -4, <i>trans</i> -5-Me ₃	100.6	80.2	78.3	20.7	17.3	17.1
2,2- <i>cis</i> -4,5-Me ₄	107.5	73.8	73.8	25.5 28.6	15.3	15.3
2,2- <i>trans</i> -4,5-Me ₄	107.8	78.5	78.5	27.1	16.9	16.9

^a Given in ppm from TMS. Benzene peak, 128.7 ppm relative to that of TMS.



Scheme 4

(+ 4.8, ppm) was used for estimating the effect of the same elongation on *trans*-4,5-dimethyldioxolane: 78.9 + 4.8 = 83.7 ppm. The influence of the structural change is usually detectable only for the chemical shift of the α , β , and γ carbons.¹⁷ Thus, the chemical shift of the acetal methylene is unaffected at 94.0 ppm. Additional chain elongation gives the chemical shift of the substituted ring carbon in the *n*-propyl derivative at 81.4 ppm. Figure 2 shows the calculated chemical shift for the various polymer structures which can be expected from the polymerization process depicted in Schemes 2 and 3.

The presence of peak k and peaks g and h in the polymer spectrum strongly suggests the formation of structure **XI** of Figure 2. The calculated peak positions for structure **XII** are also not inconsistent with these peaks. However, the separation of peaks g and h (1 ppm) appears too small for the presence of the two steric isomers (**XI** and **XII**), since a chemical shift difference of 4.8 ppm was found between *cis*- and *trans*-4,5-dimethyl-1,3-dioxolanes. The assignment of peaks i and j to the ring methyne carbon of structure **XII** is also unlikely, as will be discussed

later. Thus, the formation of structure **XII** is considered unlikely, though not excluded totally. Simple six-membered structures (**XIII** and **XIV**) can be discarded because there is no polymer peak at *ca.* 36 ppm (expected for structure **XIII**) or at *ca.* 87 ppm (expected for structure **XIV**). Branched structures **XV–XVII** could be formed by hydrogen abstraction by the methylenedioxolane radical from the 2-position of the ring and the subsequent propagation at the 2-position (see Scheme 2). Similarly, structures **XVIII** and **XIX** could be formed from the six-membered radical as shown in Scheme 3. The polymer spectrum is not compatible with these structures because some of the expected peaks are absent: a peak at *ca.* 100 ppm for **XV–XVII** and a peak at *ca.* 60–67 ppm for **XVIII** and **XIX**.

The peak observed at 14.0 ppm is in the methyl carbon region.¹⁷ There are several possibilities for the formation of the methyl group. One of them is the formation of structures related to **XV–XVII**, but this is readily excluded by the above discussion. A second possibility is the methyl group of the initiator fragment. However, this peak is too large for a terminal group of the polymer of $\bar{M}_n = 7700$. Furthermore, the methyl carbon of the cyanoisopropyl group is estimated to be at 33–36 ppm (not at 14 ppm)²⁴ and no peak corresponding to the cyano carbon at 122–125 ppm is present. The remaining possibility is the formation of a ring structure analogous to those of **XX** and **XXI**. These structures would be formed by hydrogen abstraction from the adjacent methylene group by the methylenedioxolane radical of Scheme 2. The calculated shifts for the methyl carbon and the two ring-methyne carbons of structure **XX** correspond nicely to the

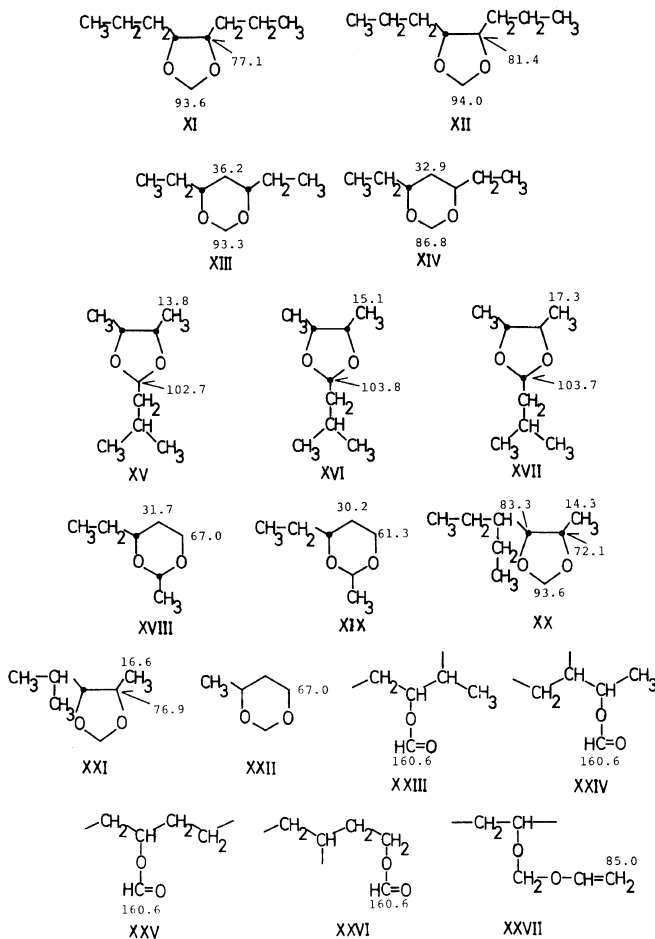


Figure 2. Calculated chemical shifts for the conceivable structural units in poly(divinyl formal).

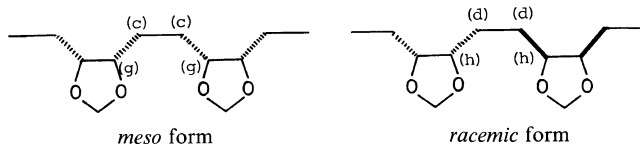
positions of the observed peak a, f, i, and j. In addition, the areas for peaks a and i+j are approximately the same (1 : 1.1), in consistence with structure XX.

If this assignment for peaks i and j is correct, then the occurrence of structure XII can be excluded, although there remains the possibility that these peaks are partly derived from the ring-methylene carbon of structure XII.

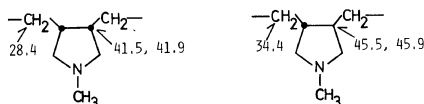
The presence of two twin peaks (c and d, and g and h) may be explained by stereoisomerism in the

connection of two *cis*-dioxolane rings. The methylene dioxolane unit can be connected either in the *meso* or *racemic* form.

The methylene and methyne carbons of the *meso* form will experience greater steric compression than those of the *racemic* form, with a resulting high-field shift. Thus, the assignments were made as indicated in the above structures. These two forms are present in approximately equal amounts. A similar example has been reported for poly(*N*-substituted diallylamine)s.²⁵ The ring-methylene peak of the *cis-N*-



methylpyrrolidine ring is split into two peaks at 41.5 and 41.9 ppm and that of the *trans*-ring into two at 45.5 and 45.9 ppm. However, such splitting was not found for the exocyclic methylene group.



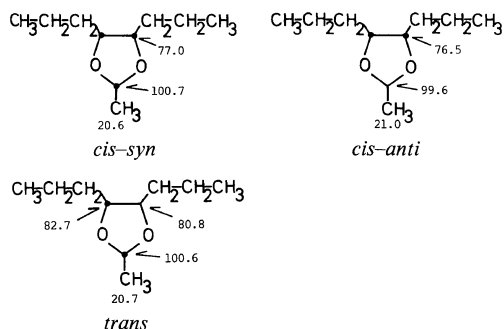
Similar splittings were found for other *N*-substituted polymers, but not for quaternized polymers.²⁶

Structures of Poly(acetaldehyde divinyl acetal) and Poly(acetone divinyl acetal)

IR spectra of these polymers indicate the absence of the pendent double bond and of the ester group. The radical rearrangement which leads to the formation of the ester group is of course impossible in the case of poly(acetone divinyl acetal). ¹³C NMR spectra of these polymers are shown in Figures 3 and 4. These spectra resemble that of poly(divinyl formal) except for the acetal methyl peaks at *ca.* 20 ppm (Figure 3) and at 25–30 ppm (Figure 4). Therefore, the cyclized structure was concluded to consist almost exclusively of the *cis*-dioxolane ring. The presence of the methyl peak again indicates the frequent occurrence of branching reaction.

The 2-methyl group in poly(acetaldehyde divinyl

acetal) may be either in the *syn* or *anti* form. The chemical shifts for the model compounds of these stereoisomers were estimated as follows.



The observed shift is 20.5 ppm for the 2-methyl carbon, 77.8 and 78.9 ppm for the 4-methylene carbon, and 100.5 ppm for the 2-methylene carbon.

Although the chemical-shift differences between the model compounds are small, the observed data (2-methyl and 2-methylene particularly) agree remarkably well with those of the *cis-syn* isomer. In fact, the *cis-syn* isomer has been concluded to be more stable than the *cis-anti* isomer based on the total chemical shift and other physical constants.^{14,16} Preferential formation of the *syn* isomer was also noted in the acetalization reaction. The final assign-

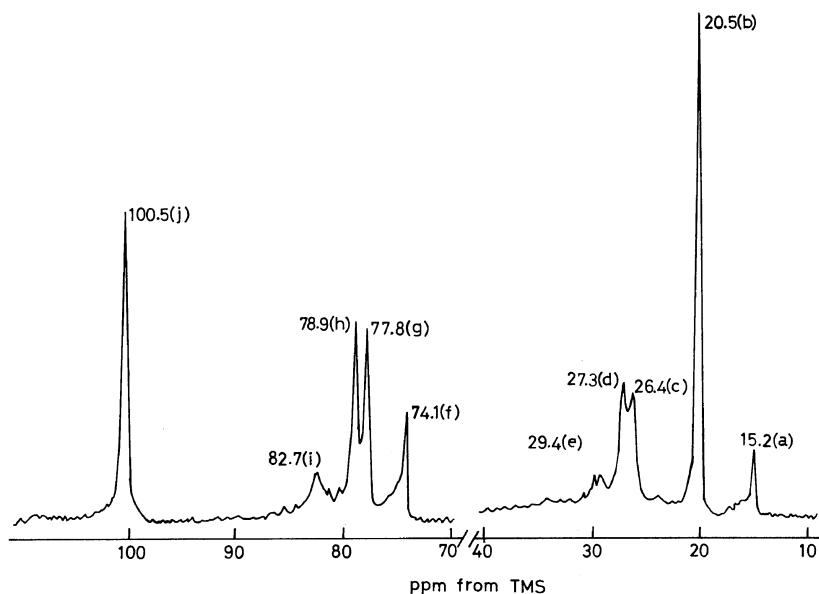


Figure 3. ¹³C NMR spectrum of poly(acetaldehyde divinyl formal). 40 wt% in C₆D₆/C₆H₆. Internal reference, benzene.

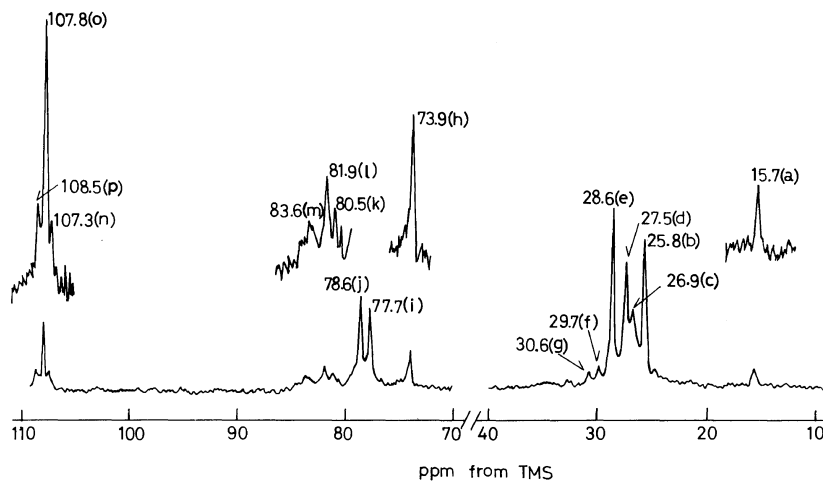


Figure 4. ^{13}C NMR spectrum of poly(acetone divinyl formal). 40 wt% in $\text{C}_6\text{D}_6/\text{C}_6\text{H}_6$. Internal reference, benzene.

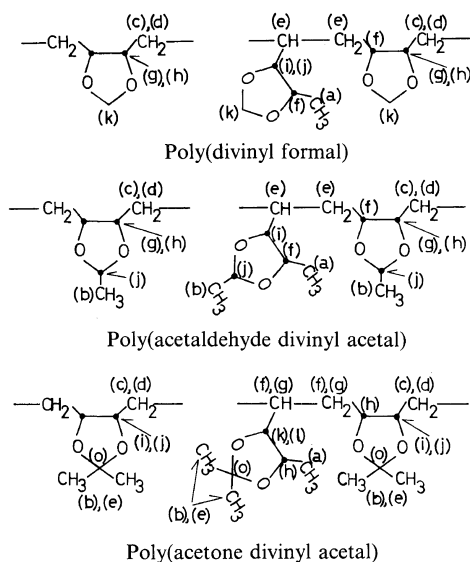


Figure 5. ^{13}C NMR assignments. See Figures 1, 3, 4 for the peak positions.

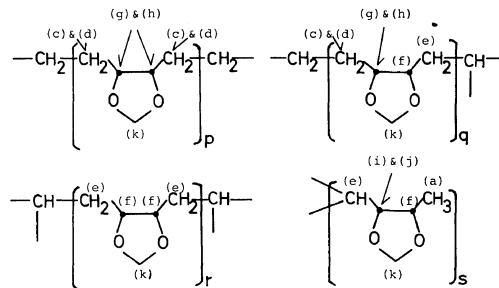
ments for the three polymers are summarized in Figure 5.

Sequence Distribution

From the above assignments, all the polymers are shown to be made of two structural units: the *cis*-cyclized dioxolane ring and the pendent dioxolane ring. The distribution of these two units along the polymer chain can be estimated from the relative NMR peak area. This procedure will be explained by

using poly(divinyl formal) as example.

The following four structures can be differentiated from the NMR data.



The peak assignments for all the carbons are given as shown above. Branching causes down-field shifts of *ca.* 3 ppm on the β -carbon and up-field shifts of *ca.* 3 ppm on the γ -carbon. These effects were taken into account in the assignment of peaks c to h. The small peak b could not be assigned to any specific carbon.

The nuclear Overhauser enhancement in polymers is considered to be fairly constant for all the carbons, with the probable exception of the quaternary carbon.^{27*} The relative peak area can be related to the fraction of each structural unit (*p*, *q*, *r*, and *s*) as given in Table III.

* In fact, the fraction of the branched structure *s* estimated by using peak k (quaternary, acetal carbon) in poly(acetone divinyl acetal) was quite different from that estimated by using the methyl peak area (peak a) of the same polymer. Therefore the latter value was adopted.

Table III. Relative peak area

Theoretical ^a	Observed ^b
Peak area (a)=Peak area (i & j)= <i>s</i>	0.06
Peak area (c & d)=Peak area (g & h)=2 <i>p</i> + <i>q</i>	0.22
Peak area (e)=Peak area (f)= <i>q</i> +2 <i>r</i> + <i>s</i>	0.08–0.10
Peak area (k)= <i>p</i> + <i>q</i> + <i>r</i> + <i>s</i>	0.24

^a Peak areas are normalized.

^b The value is given relative to the sum of all the peak areas.

Table IV. Fraction of each structural unit^a

Polymer	<i>p</i>	<i>q</i> + <i>r</i>	<i>s</i> (pendent)
poly-DVF	0.65	0.10	0.25
poly-CH ₃ -DVA	0.64	0.11	0.25
poly-2CH ₃ -DVA	0.63	0.19	0.17

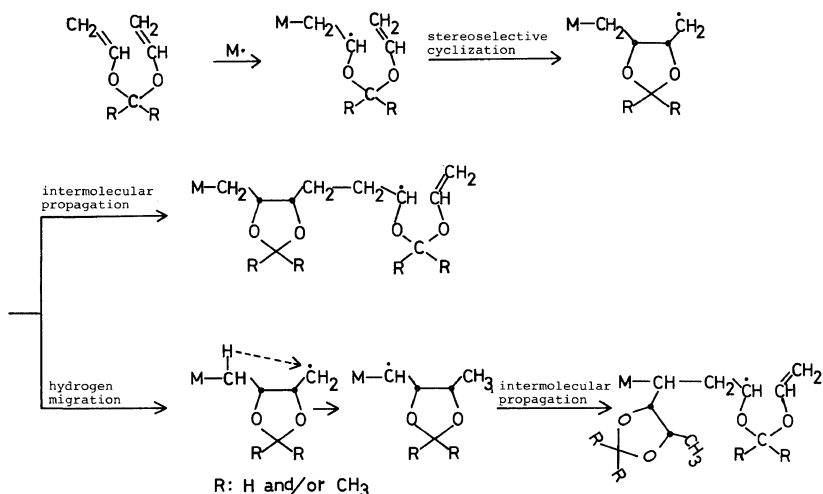
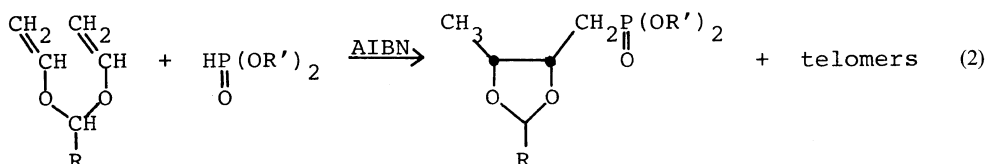
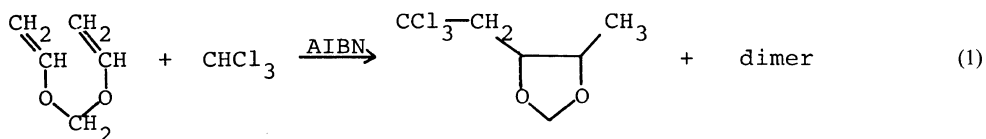
^a Estimated from the data of Table III.

The observed peak area is given as an averaged value when two peaks were used for estimation of theoretically the same area. The fraction of each structural unit was calculated from the relations of Table III and is given in Table IV. Similar calculations were made also for the other two polymers. It should be cautioned however that these values are only semiquantitative because of the presence of a large variety of the carbon atoms and of poor peak separations in several cases.

The fraction of the pendent dioxolane ring (fraction *s*) is 0.25 for poly(divinyl formal) and for poly(acetaldehyde divinyl acetal), and 0.2–0.3 for poly(acetone divinyl acetal). Since *q*+*r* are much smaller than *p*, the branched structure appears to exist in blocks instead of in a random distribution.

Polymerization Scheme

The propagation process of divinyl formal and divinyl acetals in bulk or in benzene may be sum-



Scheme 5

marized as shown by Scheme 5. The cyclization reaction yields almost exclusively the *cis*-dioxolane ring, and the methylenedioxolane radical either adds to another monomer or abstracts hydrogen from the neighboring methylene group to form a pendent dioxolane ring.

Previously, Aso, *et al.*,⁹ reported the exclusive formation of the dioxolane ring in the radical telomerization of divinyl formal and chloroform (eq 1). Gavrilova, *et al.*,²⁸ showed that the cyclic adducts of divinyl acetals and dialkyl phosphinate (AIBN initiator) contained 93–95% of the *cis*-dioxolane ring (eq 2).

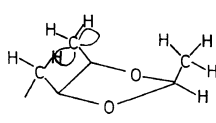
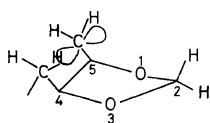
However, the ring size and stereochemistry of the cyclized unit have not been established in the polymerization system. The present study determined the microstructure of the cyclized unit in poly(divinyl acetal)s for the first time.

It is reported that *cis*- and *trans*-substituted pyrrolidine rings are contained in the ratio of *ca.* 5 : 1 in the cyclopolymers of *N,N*-diallylamines.^{25,26} This result is a little different from the exclusive formation of the *cis*-dioxolane ring from divinyl acetals.

In both cases, the formation of the *cis* ring is favored kinetically, but the *trans* ring should be favored thermodynamically. The difference in the ring strain between the *cis* and *trans* structures is considered to be somewhat greater for pyrrolidines than for dioxolanes, as discussed below. Because of this thermodynamic factor, some amounts of the *trans* structure would become involved in the cyclized unit of poly(diallylamine)s.

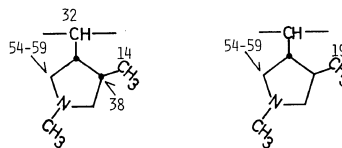
The formation of the pendent dioxolane unit (17–25%) was totally unexpected. Although the hydrogen abstraction from the 2-position has been discussed (see Scheme 2), the abstraction from the neighboring methylene has not been mentioned in the literature.

In the space-filling (CPK) molecular model of the *cis* methylenedioxolane unit, the radical p orbital overlaps readily with the hydrogen orbital of the 4-methylene group; however, the hydrogens at the 2-position and at the 2-methyl substituent are too far away for the overlapping, as seen in the following.

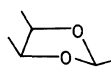


Therefore, the present finding is consistent with the inference from the molecular model.

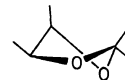
In the ¹³C NMR spectrum of poly(methyldiallylamine), there were several minor peaks (14 and 19 ppm) which were tentatively assigned to the terminal structures.²⁵ However, we believe that these small peaks should be assigned to the following structures, which were formed by hydrogen abstraction as in the polymerization of divinyl acetals, although the pendent *trans* pyrrolidine ring is less likely due to limited orbital overlapping during hydrogen migration.



These small peaks cannot be found in the spectrum of poly(dimethyldiallylammonium chloride).²⁶ This result is in line with the fact that the content of the isomerized structure is a little smaller in poly(acetone divinyl acetal) than in the other divinyl acetal polymers. The dihedral angle of the *vicinal cis* hydrogens at the 4 and 5 position is 35° in the envelope conformation of 1,3-dioxolane. On the other hand, the dihedral angle for the 2,2-dimethyl derivative is 41° because the skewed conformation becomes favorable.²⁹ Some chemical shift differences between the *vicinal* dimethyl groups of the *cis* and *trans* isomers are collected in Figure 6 from ref 21, 25, 26, and the present study. In the first, the shift difference for the dioxolanes is smaller than that for cyclopentanes and pyrrolidines, reflecting the flexibility of the dioxolane ring.¹⁴ Secondly, the shift difference becomes smaller as the methyl substituent at the 2-position increases. Therefore, the *vicinal* methyl groups are less eclipsed in the 2,2-dimethyldioxolane than the unsubstituted counterpart. The same conclusion is reached for the pyrrolidine derivatives. Lessened eclipsing of the 4 and 5 substituents would naturally lead to less hydrogen migration in the dioxolane intermediate.



eclipsed conformation



skewed conformation

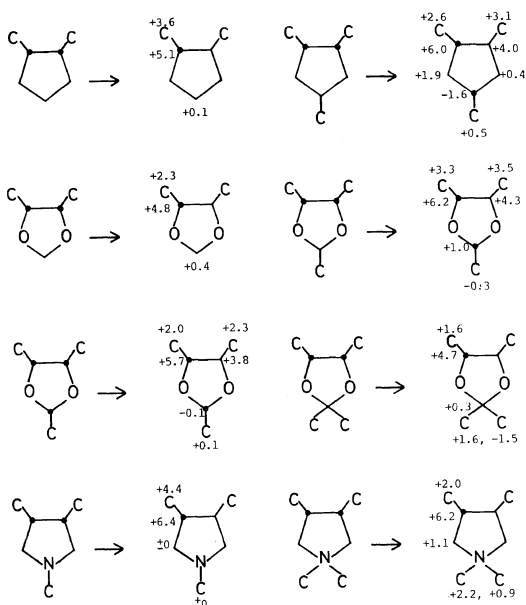


Figure 6. Chemical-shift differences between the *cis* and *trans* isomers of five-membered ring compounds with vicinal dimethyl substitution.

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