Radical Cyclopolymerization of Divinyl Ether. The Microstructure of the Polymer and the Cyclopolymerization Mechanism[1]

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ABSTRACT: Radical polymerization (AIBN initiator) of divinyl ether yielded partially cyclized, soluble polymers. The pendent vinyloxy group could be completely removed by treating the polymers with 2% hydrochloric acid in methanol. Based on ^{13}C-NMR spectra of these polymers, the original polymer was concluded to contain a five-membered monocyclic unit with the pendent vinyloxy group and a bicyclic unit (dioxobicyclo[3.3.0]octane system) in the 1:1 ratio. The carbon chemical shifts expected for all the possible stereoisomers of these structural units were estimated using a number of model compounds. Apparently a single stereoisomer was formed for both the monocyclic unit (trans ring closure) and the bicyclic unit (with the trans junction). Finally, the steric course of the cyclopolymerization was compared with those of the related systems.

Divinyl ether undergoes radical polymerization to produce soluble polymers with highly cyclized structures.[2] Aso et al.[3] proposed that the polymer contained bicyclic structures and uncyclized units, and Guaita et al.[4] suggested the presence of the monocyclic and bicyclic structures on the basis of kinetic and stereochemical considerations. Recently, we reported briefly that among many conceivable structural units shown in Figure 1, the polymer contained an unsaturated unit S_{50} and a bicyclic unit S_{55} in the 1:1 ratio.[5] In this paper, we describe the structure determination of the polymer in detail. The stereochemistry of the cyclic unit is also described, and the cyclopolymerization process is discussed based on these structural data.

Experimental Section

Materials. Divinyl ether (Japan Oil Seal Co.) was washed with aqueous alkali and water, dried over KOH, and distilled from CaH_2, bp 27–28 °C. Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Bicyclo[3.3.0]octane (Chemical Sample Co.) was confirmed to be sufficiently pure by gas chromatography (impurity peak less than 1%): mp −52 to −50 °C (lit.[6] mp below −80 °C (cis isomer), −30 °C (trans isomer)); d^{18}_4 0.8703, d^{16}_4 0.8721 (lit.[6] d^{18}_4 0.8716 (cis isomer), d^{16}_4 0.8648 (trans isomer)). The bicyclooctane was concluded to be in the cis configuration from these data. Solvents were purified in the usual procedure.

Polymerization. Given amounts of monomer, AIBN, and solvent were placed in ampules and subjected to the freeze–pump–thaw cycle several times. The ampules were then sealed in vacuo and immersed in a polymerization bath. The polymer was recovered by precipitation in methanol, purified by reprecipitation from benzene and methanol, and freeze-dried. The polymers were white powders and soluble in many common solvents when not cross-linked. The polymerization results are summarized in Table I. Gelation occurred frequently at higher polymerization temperatures or at greater conversions. The amount of the residual double bond was determined by ^{1}H-NMR spectroscopy (CCl_4 solvent, Varian A60 instrument) from the relative peak area of the vinyl methine proton (6.0–6.6 ppm) and the total proton.

Hydrolysis. Two grams of the polymer (Table I, run 1) were dissolved in 9 mL of benzene which contained a trace amount of 2,6-di-*tert*-butylcresol, and 7 mL of 2% hydrochloric acid in methanol was slowly added with stirring. The homogeneous solution thus obtained was stirred further for 40 min and then poured into 300 mL of ether. White powdery precipitates were filtered and dried, yield 1.4 g. Anal. Calcd for $(C_4H_6O)_{0.73}$-$(C_2H_4O)_{0.27}$: C, 65.90; H, 8.73. Found: C, 65.04; H, 8.79.

Miscellaneous. ^{13}C-NMR spectra were obtained using a 22.63-MHz Bruker FT-NMR instrument under noise decoupling: pulse delay time, 10 s; flip angle, 23°; spectral width 4000 Hz; accumulation, 6000 scans.

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Table I
Selected Examples of Radical Polymerization of Divinyl Ether[a]

run no.	AIBN mol % of monomer	temp, °C	time, h	conversion, %	PDB,[b] %	$\bar{M}_n$
1	0.45	70	6	28[c]	28	61 000
2	0.50	50	44	24	26	32 000
3	1.00	60	7	23	24	19 000

[a] Monomer: 20 wt % in benzene. [b] Content of the pendent double bond. PDB is 100% when each monomer unit contains one vinyl group. [c] Anal. Calcd for C_4H_6O: C, 68.53; H, 8.64. Found: C, 69.03; H, 8.66.

Results and Discussion

Location of the Pendent Double Bond. Figure 2 shows a ^{13}C-NMR spectrum of poly(divinyl ether), together with that of the hydrolyzed product. The spectrum of the original polymer is made of at least 11 peaks. From comparison with published data,[7] peaks (a) to (e) are assigned to aliphatic methylene carbons, and peaks (f) to (i) are assigned to the aliphatic methylene and methine carbons adjacent to the ether oxygen. Peaks (j) and (k) are assigned to the methylene and methine carbons of the pendent double bond, respectively.

Upon hydrolysis, peaks (j) and (k) diappeared completely in agreement with the above assignment. Furthermore, peak (g) shifted to higher field by 7.1 ppm, and peaks (d) and (h) shifted to lower field by 2.3 and 2.7 ppm, respectively. Other peaks were affected little by the hydrolysis. Generally speaking, when a secondary alkyl vinyl ether is converted to the corresponding secondary alcohol, the peak of the α carbon moves to higher field by ca. 6 ppm and that of the β carbon to lower field by ca. 3 ppm, whereas the γ carbon is not affected.[7,8] Therefore, peak (g) is assigned to the carbon adjacent to the pendent vinyloxy group (α carbon) and peaks (d) and (h) to the β-methylene and β-methine carbons, respectively. The vinyloxy group may be a part of the uncyclized unit or it may be attached to the five- and/or six-membered cyclic unit.

The carbon chemical shifts of these structures can be estimated from those of appropriate model compounds. In the case of the S_{50} structure, the ^{13}C-NMR data for substituted tetrahydrofurans were compared with those

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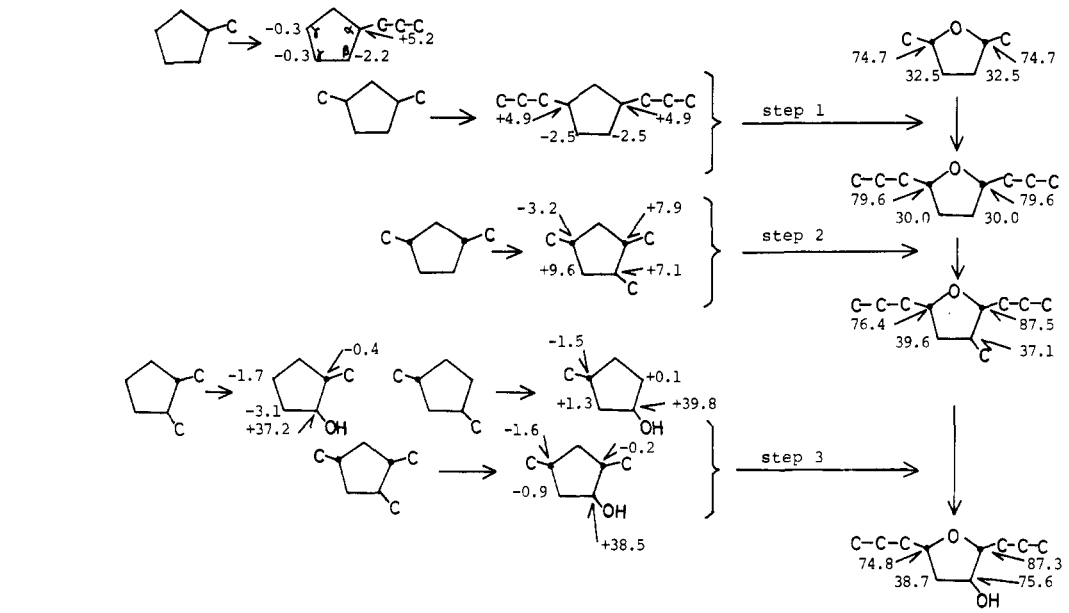
Scheme I



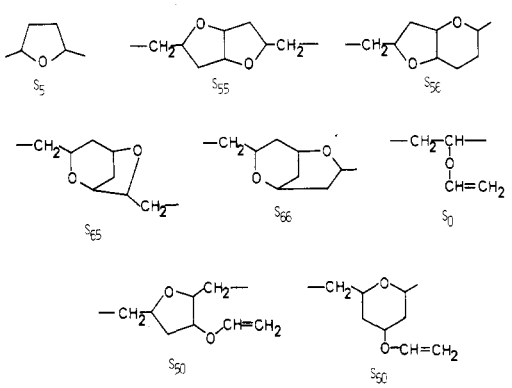


Figure 1. Conceivable structural units of poly(divinyl ether).

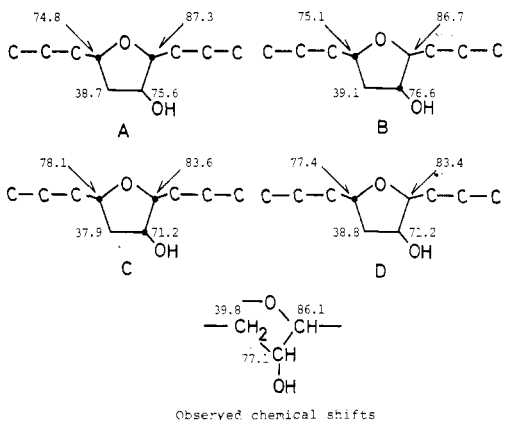


Figure 3. Comparison of the observed chemical shift of the hydrolyzed polymer with those estimated for 2,5-dipropyl-3-hydroxytetrahydrofurans.

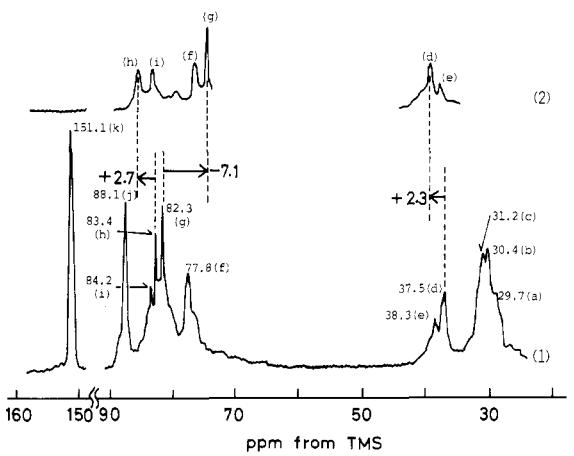


Figure 2. ^{13}C-NMR spectra of poly(divinyl ether) and its hydrolysis product. The peak shift upon hydrolysis is indicated by arrows. Internal reference, Me_4Si: (1) poly(divinyl ether), sample Table I, run 1, 40 wt % in C_6D_6; (2) hydrolyzed polymer, 23 wt % in C_6D_6/CH_3OH.

of the hydrolyzed polymer, because the data for the corresponding vinyl ethers could not be found in the literature. An example of the procedure is given in Scheme I. The reported chemical shifts for alkylcyclopentanes[9,10] and cyclopentyl alcohols[10] were used for the derivation. The chemical shifts for dimethyltetrahydrofurans were measured in the present study.

In Scheme I transformation of methylcyclopentane to *n*-propylcyclopentane produces a downfield shift of 5.2 ppm at the substituted ring carbon (α carbon) and upfield shifts of 2.2 and 0.3 ppm for the β and γ carbons, respectively. These effects were used in estimating the chemical shift difference between 1,3-dimethylcyclopentane and 1,3-di-*n*-propylcyclopentane, e.g., +5.2 − 0.3 = +4.9 ppm. The resulting differences (+4.9 and −2.5 ppm for the α and β carbons) were added in step 1 to the chemical shift of *cis*-2,5-dimethyltetrahydrofuran in order to estimate the chemical shift for *cis*-2,5-di-*n*-propyltetrahydrofuran, e.g., 74.7 + 4.9 = 79.6 ppm for the α carbon. The subsequent operations involve introduction of the 3-methyl substituent and its conversion to the hydroxyl substituent. The calculated chemical shifts are thought to be reliable within 2-3 ppm, judging from differences in the chemical shift among closely-related model compounds.

Four configurational isomers are present for 2,5-di-*n*-propyl-3-hydroxytetrahydrofuran, and the chemical shifts of the ring carbon of these isomers were estimated by a procedure similar to that shown in Scheme I. These results are summarized in Figure 3, together with the observed shifts. It is clear that structures A and B are more consistent with the observed shifts than structures C and D. The observed chemical shift of the hydroxyl-substituted

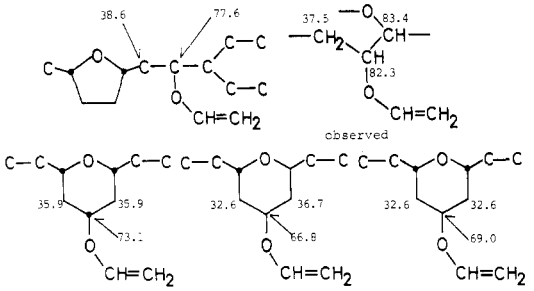


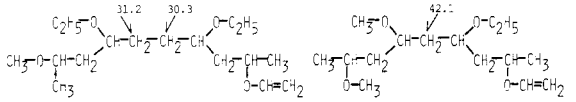
Figure 4. Comparison of the observed chemical shift of poly(divinyl ether) with those estimated for some of the structural unit with the vinyloxy substituent.

methine carbon agrees with those of structures A and B within 1.5 ppm. In contrast, the corresponding difference with structures C and D is ca. 6 ppm, a value much greater than is allowed by the estimated error of the procedure. Structures A and B give better agreements also for the chemical shift of the 2-carbon.

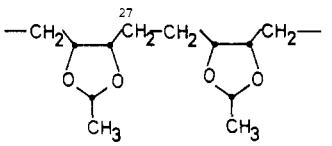
The chemical shift for the uncyclized structure (S_0) connected to a tetrahydrofuran ring was estimated on the basis of the chemical shift of alkylcyclopentanes,[9,10] methyltetrahydrofurans,[11] and dimethyltetrahydrofurans using a procedure similar to that given in Scheme I. The chemical shift for the model compound of structure S_{60} was also derived using the data of alkylcyclohexanes,[9,12] methyl-substituted tetrahydropyrans,[13] and cyclohexyl vinyl ether.[14] As can be seen from Figure 4, these structures do not give chemical shifts which are compatible with the observed values.

Structure of the Bicyclic Unit. The initial clue for the determination of the bicyclic structure was the chemical shift of the exocyclic methylene group. As mentioned above, the pendent vinyloxy group is present in the form of the S_{50} structure. Since the content of the pendent vinyloxy group is 25–28% (this value is 100% when only one of the vinyl groups is consumed in the polymerization), the monocyclic S_{50} unit and the totally cyclized (bicyclic) unit must be contained in approximately 1:1 ratio. When the S_{50} structure is connected to the S_{65} or S_{55} structure, only the exocyclic ethylene unit is formed. On the other hand, if S_{50} is connected to S_{56} or S_{66}, both of the exocyclic ethylene and methylene units will be formed. The combination of S_{50} with S_5 will yield only the exocyclic methylene unit.

The chemical shifts of the exocyclic ethylene unit and the isolated exocyclic methylene unit of the appropriate model compounds can be readily estimated from the rule of Lindeman and Adams on branched alkanes[15] and from the effect of the group transformation, as given below.



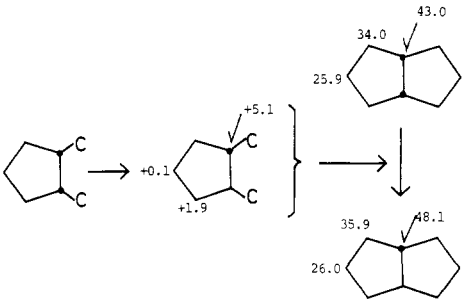
The peak of the exocyclic ethylene carbon of poly(acetaldehyde divinyl acetal) is located at 27 ppm.[16] If the steric compression effect due to the cis substitution is relieved in this polymer, the peak should shift to 30–31 ppm, in consistence with the above estimation.



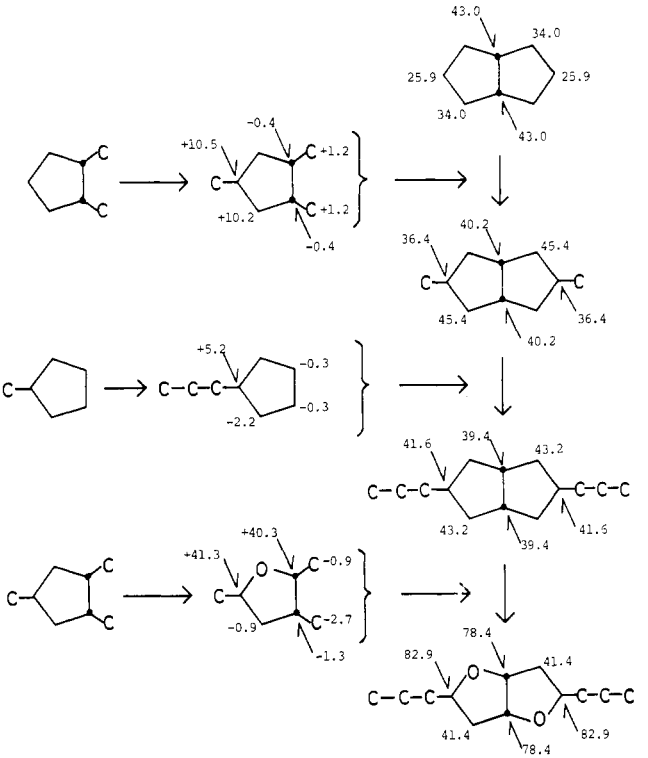
In the polymer spectrum of Figure 2, peak (d) at 37.5 ppm has been assigned to the ring methylene carbon of S_{50}, and peak (e) at 38.3 ppm is attributed to the ring methylene carbon which is in the β position relative to the ether oxygen of the bicyclic structure as discussed later. Therefore, peaks attributable to the exocyclic *methylene* unit at ca. 40 ppm are absent in the polymer spectrum, and peaks (a) to (c) at 29.7–31.2 ppm must be assigned to the exocyclic *ethylene* group. It is concluded from these discussions that structure S_{50} is connected to S_{55} and/or to S_{65}.

Peak (e) is assignable to the ring methylene carbon of the bicyclic structure. Peaks (f) to (j) are attributed to the methine carbon. Peak (f) split into two sharp peaks when the spectrum was measured in $CDCl_3$ solvent. Among these six peaks, peaks (g) and (h) shifted upon hydrolysis and were assigned to the methine carbon of S_{50} structure. Peak (j) belongs to the methine carbon of the pendent vinyloxy group. One of the peaks which (f) split into is attributed to the ring methine carbon which is in the γ position relative to the vinyloxy group. Therefore, only two peaks should belong to the methine carbon of the bicyclic structure. The S_{65} structure, being unsymmetrical, would give rise to two kinds of ring methylene carbon and four kinds of ring methine carbon, even if the configuration is constant. In contrast, the S_{55} structure of the constant configuration would yield one kind of ring methylene

Scheme II



Scheme III



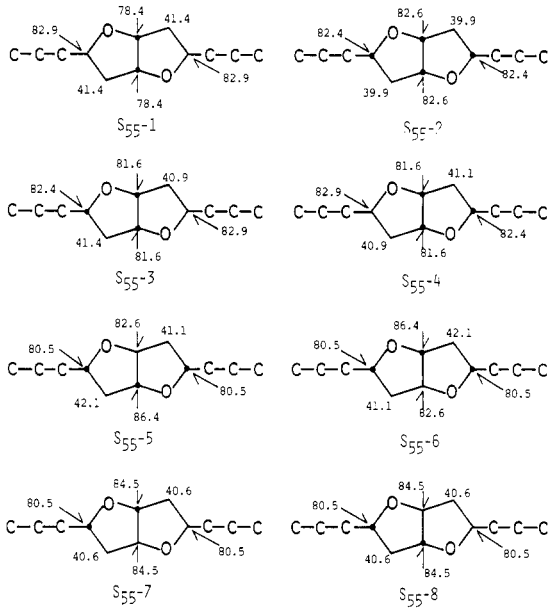


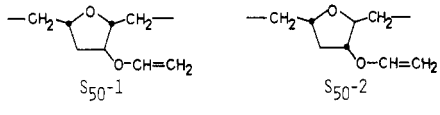
Figure 5. Carbon chemical shifts estimated for all the configurational isomers of 3,7-di-*n*-propyl-2,6-dioxobicyclo[3.3.0]octane.

carbon and two kinds of ring methine carbon.

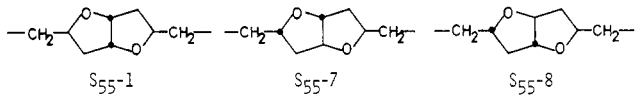
These considerations strongly suggest that the bicyclic structure is the symmetrical S_{55} structure, and its configuration can be inferred by comparison of the observed chemical shifts with those of appropriate model compounds: *cis*-bicyclo[3.3.0]octane, alkylcyclopentanes,[9] and methyltetrahydrofuran.[11] The chemical shifts for *cis*-bicyclo[3.3.0]octane were obtained in this study, and those of the trans isomer were estimated using the data for the cis isomer and for dimethylcyclopentane isomers,[9] according to Scheme II. Scheme III illustrates the procedure for estimating the chemical shift for one of the stereoisomers of the model structure corresponding to S_{55}. The same procedure was applied to other configurational isomers.

Eight configurational isomers are conceivable for the S_{55} structure as shown in Figure 5, if the direction of propagation is fixed.[17] The direction of propagation cannot however be differentiated in the polymer spectrum, and two pairs of the structure would give rise to identical spectra: S_{55}-3 and S_{55}-4, S_{55}-5 and S_{55}-6. Among the remaining six structures, less symmetrical S_{55}-3 and S_{55}-5 would give too many methylene and methine peaks to be compatible with the observed spectral simplicity, and the calculated chemical shift of S_{55}-2 is not consistent with the observed spectrum. Thus, S_{55}-1, S_{55}-7, and S_{55}-8 remain as candidates for the bicyclic structure.

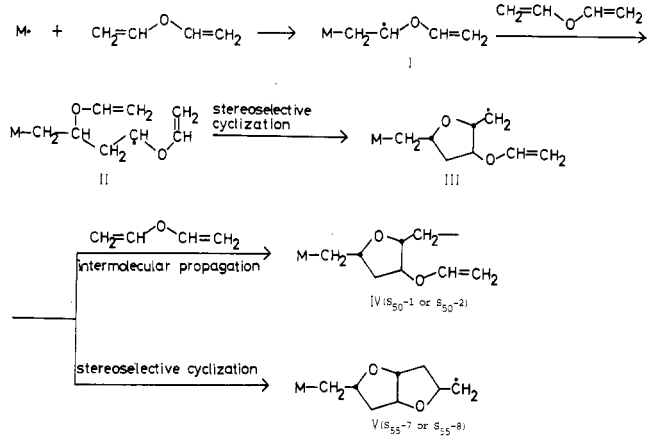
Polymer Structure. The preceding analysis of the ^{13}C-NMR spectrum indicates that the polymer contains approximately equimolar amounts of the monocyclic unit (S_{50}-1 and/or S_{50}-2) and the bicyclic unit (S_{55}-1, S_{55}-7, and/or S_{55}-8). Monocyclic unit:



Bicyclic unit:



Scheme IV

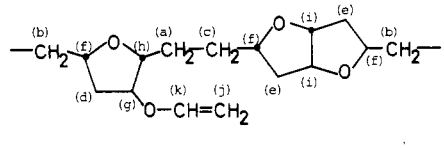


Considering the limited number of NMR peaks, only one kind of each structural unit (monocyclic and bicyclic) appears to be contained in the polymer.

The amount of the pendent double bond was reported to increase with the monomer concentration.[4] The configuration of the monocyclic unit should be independent of the monomer concentration, since the cyclization process is an intramolecular reaction. The bicyclic unit is naturally formed via the monocyclic unit. If the two configurationally isomeric monocyclic intermediates are formed, and if one of the intermediates yields the bicyclic unit exclusively and the other undergoes the exclusive intermolecular propagation, then the amount of the pendent vinyloxy group would again be independent of the monomer concentration. This is not compatible with the experimental data. In the second case, if the two kinds of the monocyclic intermediate are formed and both of them give rise to the bicyclic unit partially, the polymer will contain two each of the monocyclic and bicyclic structures. This again contradicts the spectral data. Considering the spectral simplicity, the monocyclic and bicyclic units must have the same configuration. Then, the cis-fused bicyclic unit S_{55}-1 cannot be reconciled with the steric configuration of the monocyclic unit and is discarded.

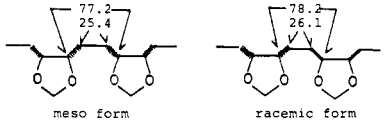
The most plausible mechanism of the cyclopolymerization is as follows: only one kind of monocyclic intermediate is formed by the trans ring closure. This intermediate reacts with monomer to yield the monocyclic unit or undergoes the intramolecular cyclization stereoselectively to form a bicyclic unit in which the exocyclic methylene radical is in the anti position with respect to the preceding cyclic unit. Then, the polymer may be composed either of S_{50}-1 and S_{55}-7 or of S_{50}-2 and S_{55}-8. These two possibilities cannot be differentiated spectrally.

The final spectral assignment is given below using the combination of S_{50}-1 and S_{55}-7.



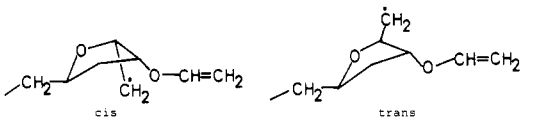
These cyclic units can also be in the corresponding enantiomeric forms. Then, the connection of the two cyclic units will be in the meso-like form as given above or in the racemic form. This stereochemical difference may give rise to spectral discrimination. In fact, two types of exocyclic ethylene unit were noted in the ^{13}C-NMR spectrum of poly(divinyl acetals)[16] and poly(diallyl amines).[18] The

different chemical shifts for the two forms in poly(divinylformal) is illustrated below as an example.

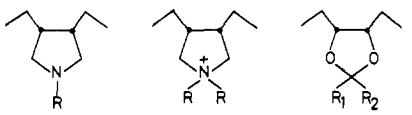


In the ^{13}C-NMR spectrum of poly(divinyl ether), the exocyclic methylene peaks (a)–(c) are not well resolved, and peaks (f) and (g) are fairly sharp. Therefore, this problem cannot be discussed further.

Steric Course of Cyclopolymerization. Scheme IV summarizes the cyclopolymerization process of divinyl ether including stereochemistry. The head-to-tail addition of monomer to the uncyclized radical I gives radical II, which cyclizes stereoselectively to monocyclic radical III. Although the steric relation of the penultimate substituent and the newly formed ring juncture is not determined (both S_{50}-1 and S_{50}-2 are possible), the trans ring closure occurs selectively in the monocyclization step. As shown below, if the penultimate group is placed in the equatorial position, both the methylene radical and vinyloxy groups in the cis-fused ring would be in the axial position and considerable steric repulsion might arise. This situation is relieved by placing the vinyloxy group in the equatorial position via the formation of the trans junction.

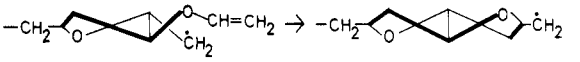


The trans ring closure contrasts with the cis, head-to-head cyclization of some 1,6-diene monomers. For instance, the cis-substituted pyrrolidine was the predominant structural unit in the polymer of diallylamines[18] and diallylammonium salts.[19] The exclusive formation of the cis dioxolane ring was found in the polymerization of divinyl acetals.[16] Therefore, the cis ring closure must be kinetically favored in the cyclopolymerization of unsubstituted 1,6-dienes.



It appears that the steric factor of the penultimate unit exerts greater influence than the kinetic preference of the cis closure of the five-membered ring in the monocyclization step of Scheme IV.

The monocyclic radical III will either add to monomer or cyclize stereoselectively to form a bicyclic radical V. The two competing processes occur in almost the same ratio. The *trans*-bicyclo[3.3.0]octane is considered to be in the skew conformation.[6] The corresponding dioxo skeleton should be more flexible,[20] and the bicyclic unit with trans junction will be formed fairly readily.



Conclusion

We could determine the microstructure of poly(divinyl ether) fairly definitely in this study. ^{13}C-NMR spectroscopy was a very powerful tool for this purpose when coupled with the extensive use of model compounds. In the last few years, the stereochemistry of cyclopolymerization has been elucidated increasingly by ^{13}C-NMR spectroscopy. Therefore, we may expect to reach unified understanding of the geometrical and stereochemical features in cyclopolymerization.

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