Radical Cyclopolymerization of Divinyl Acetals—Structure Variation with Polymerization Conditions[†]

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ABSTRACT: Radical polymerizations of divinyl formal, acetaldehyde divinyl acetal, and acetone divinyl acetal were conducted under a series of conditions, and the microstructures of the cyclopolymer obtained were examined by ¹H NMR and ¹³C NMR spectroscopies. The cyclopolymer contained *cis*-dioxolane units as the major structure along with other minor structures such as the pendant dioxolane unit and *trans*-dioxolane unit. The content of the major structure increased with lowering polymerization temperature and increasing monomer concentration. The uncyclized unit and the six-membered dioxane ring were not formed under any condition. The propagation steps included cyclization and isomerization in addition to monomer addition and are discussed on the basis of variation in polymer structure with polymerization conditions. The methyl substitution at the acetal carbon lowers isomerization of the cyclized radical.

KEY WORDS NMR Spectroscopy / Poly(divinyl formal) / Poly(acetaldehyde divinyl acetal) / Poly(acetone divinyl acetal) / Cyclopolymerization / Steric Structure /

It has been established in the past decade that head-to-head (five-membered ring) cyclopolymer are formed by radical polymerization of non-conjugated dienes such as divinyl ethers,^{1–4} diallylamines,^{5,6} allyl esters of unsaturated acids,⁷ methacrylic anhydride,⁸ and dimethacrylamide.⁹

We studied radical cyclopolymerization of the divinyl acetal family—divinyl formal (DVF), acetaldehyde divinyl acetal (CH₃-DVA), and acetone divinyl acetal (2CH₃-DVA)—and found the polymers to be comprised of analogous structural units.¹⁰

The ¹³C NMR spectral data indicated the predominant formation of the *cis*-dioxolane ring (I), along with the pendent dioxolane unit (II) produced by intramolecular hydrogen

migration. The connection of the main structure was invariably made of equal amounts of the *meso* and *racemic* structures. No uncyclized unit or six-membered (1,3-dioxane) unit or *trans*-dioxolane units (III and IV) could be detected. These structures (I–IV) are illustrated here for DVF. The same conclusions were obtained for CH₃-DVA and 2CH₃-DVA.

More recently, for DVF it was observed that *trans*-dioxolane rings are produced under other polymerization conditions.¹¹ We thus examined the influence of polymerization conditions on the polymer structures of CH₃-DVA and 2CH₃-DVA and carried out kinetic analyses on the propagation processes of these three monomers.

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EXPERIMENTAL

Materials

Divinyl acetal monomers and 1,3-dioxolanes were prepared as described before.¹⁰ Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Organic solvents were purified by conventional methods.

Polymerization

Benzene and toluene were used as solvents for the polymerization at 10–70°C and at –10°C, respectively. AIBN was used as the initiator at 50 and 70°C, but irradiation with a 100-W high pressure Hg lamp was additionally employed for polymerization at temperatures below 30°C. Given amounts of monomer, solvent, and AIBN were placed in glass ampoules (Pyrex glass ampoules in the case of photoirradiation), which were then subjected

to several freeze-pump-thaw cycles and sealed. After polymerization in a constant-temperature bath, the contents were poured into methanol and the recovered polymers were reprecipitated from benzene and methanol. The polymers were freeze-dried if necessary. The conversions were kept below 10%.

Miscellaneous

Molecular weight was measured with a Toyo Soda HLC-802UR gel permeation chromatograph using monodisperse polystyrenes for calibration. ¹³C NMR and ¹H NMR spectra were obtained using a JEOL FX-100 spectrometer (100 MHz for ¹H and 25 MHz for ¹³C) under noise decoupling (for ¹³C).

The ¹H chemical shifts (in CCl₄) of 1,3-dioxolanes used as model compounds of the structural unit in polymers are as follows.

RESULTS AND DISCUSSION

Poly(divinyl formal)

The structural variation in poly(divinyl formal) was briefly discussed in the previous paper.¹¹ The polymerization data at various

Table I. Radical polymerization of divinyl formal in C₆H₆

Run No.	Polymn. temp	Monomer	AIBN	Polymn. time	Conversion	<i>M_n</i>
	°C	mol l ⁻¹	mol l ⁻¹	h	%	
1 ^a	–10	5.0	5 × 10 ⁻²	15.0	7.5	—
2 ^b	10	2.5	1 × 10 ⁻¹	8.0	8.6	5500
3	30	2.5	5 × 10 ⁻²	2.0	7.8	4500
4	50	2.5	1 × 10 ⁻²	20.0	7.0	14000
5 ^b	70	2.5	2 × 10 ⁻²	1.5	8.1	8100

^a Polymerized in toluene.

^b From ref 11.

Figure 1. ^{13}C NMR spectrum of poly(divinyl formal). Sample: Table I, run No. 1; 27 w/v% C_6D_6 at 75°C ; accumulation, 1000 scans.

temperatures are summarized in Table I. The molecular weights are relatively small. The polymer structure becomes more regular as the polymerization temperature is lowered. Figure 1 shows the ^{13}C NMR spectrum of the polymer obtained at -10°C . The spectrum consists of the main-chain methylene carbon (26–27 ppm), the ring methine carbon (77–79 ppm) and the acetal carbon (94 ppm). These peaks were assigned to the carbons of the main structure **I**, and the other peaks assignable to the minor structures were absent. The splitting (doublets) of the main-chain methylene carbon and ring methine carbon is attributed to the *meso* and *racemic* connections of the main structural unit.^{10,11} It is concluded that the polymer obtained at low temperatures possesses a very regular structure. The decrease in the secondary structures with increasing monomer concentrations has been mentioned before.¹¹

Poly(acetaldehyde divinyl acetal)

The polymerization results of acetaldehyde divinyl acetal are summarized in Table II. The molecular weights are higher than those of poly(divinyl formal) given in Table I. Figure 2 compares ^1H NMR spectra of the polymers obtained at different temperatures. The presence of structural units **VII** and **VIII** was confirmed from the analysis of ^{13}C NMR spectra.¹⁰ However, as with poly(DVF), the

Table II. Radical polymerization of acetaldehyde divinyl acetal

Run No.	Polymn. temp $^\circ\text{C}$	AIBN mol l^{-1}	Polymn. time h	Conversion %	M_n
1	-10	5×10^{-2}	19.0	8.8	11000
2	10	2×10^{-1}	0.5	6.4	8600
3	30	5×10^{-2}	0.6	8.7	18000
4	50	2×10^{-2}	7.0	6.0	30000
5	70	2×10^{-2}	0.5	6.0	26000

^a $[\text{M}] = 5.0 \text{ mol l}^{-1}$. Solvent, toluene for run 1 and benzene for runs 2–5.

Figure 2. ^1H NMR spectra of poly(acetaldehyde divinyl acetal). a) Sample: Table II, run No. 1. 3 w/v% in $\text{C}_6\text{D}_6 + o\text{-C}_6\text{H}_4\text{Cl}_2$ at 140°C ; accumulation, 64 scans. b) Sample: Table II, run No. 5. 3 w/v% in $\text{C}_6\text{D}_6 + o\text{-C}_6\text{H}_4\text{Cl}_2$ at 140°C .

trans ring structures **IX** and **X** could be formed by the proper selection of polymerization conditions. From comparisons with ^1H NMR

data of 1,3-dioxolanes (model compounds), the following assignments were made for the NMR spectra of Figure 2.

A (doublet), 1.60 ppm; acetal methyl proton in **X** and 5-methyl proton in **VIII**.

B (doublet), 1.75 ppm; acetal methyl proton in **VII**.

C, 2.12 ppm; exocyclic methylene and methine proton of all units.

D, 4.12 ppm; ring methine proton at the 4 and 5 positions in **IX**.

E, 4.36 ppm; ring methine proton at the 4 and 5 positions in all units other than **IX**.

F (doublet), 5.41 ppm; acetal methine proton in **VII** and **VIII**.

G, 5.57 ppm; acetal methine proton in **IX**.

The chemical shifts for the polymer protons are 0.1–0.5 ppm larger than those of the corresponding protons of the model compounds. These differences probably arise from differences in the NMR solvents (CDCl_3 for the model compounds and mixtures of C_6D_6 and *o*-dichlorobenzene for the polymers) and/or from different magnetic environments due to neighboring units of the polymer.

Since Figure 2b is less simple than Figure 2a, it is clear that the polymer obtained at a high temperature (70°C in this case) contains larger amounts of the minor structures. The above-mentioned assignments indicate that the polymer obtained at -10°C is made predominantly of structure **VII** and that other minor structures **VIII**, **IX** and **X** increase with increasing polymerization temperature.

Figure 3 gives the ^{13}C NMR spectra of poly(acetaldehyde divinyl acetals) prepared under contrasting polymerization conditions. The spectral assignments have been reported.¹⁰ The polymer obtained with a high mo-

Figure 3. ^{13}C NMR spectra of poly(acetaldehyde divinyl acetal). a) Sample: Table II, run No. 1. 27 wt% in C_6D_6 at 75°C ; accumulation, 1000 scans. b) Sample: polymer obtained in C_6H_6 at 70°C and at $[\text{M}] = 1.5 \text{ mol l}^{-1}$. 28 wt% in C_6D_6 at 75°C ; accumulation, 2000 scans.

nomer concentration at -10°C gives a simple spectrum (Figure 3a) that indicates the nearly exclusive presence of the main structural unit **VII**: B, acetal methyl carbon; C exocyclic methylene carbon; E, endocyclic methine carbon; G, acetal methine carbon. Peaks C and E are split due to the two modes of connection of the structural unit as mentioned before. In contrast, the polymer obtained with a low monomer concentration at 70°C (Figure 3b) gave additional peaks (A, D, and F) suggesting the presence of the branched structure **VIII**. The presence of the *trans* ring units **IX** and **X** was not clear in this spectrum, since peaks due to the *trans* ring units were close to those of **VIII**. However, the ^1H NMR data (Figure 2b) point to their presence.

Poly(acetone divinyl acetal)

Table III contains the polymerization results

Table III. Radical polymerization of acetone divinyl acetal

Run No.	Polymn. temp °C	AIBN mol l ⁻¹	Polymn. time h	Conversion %	M _n
1	-10	5 × 10 ⁻²	7.0	5.0	9000
2	10	2 × 10 ⁻¹	0.6	6.3	8100
3	30	5 × 10 ⁻²	0.4	9.3	13000
4	50	2 × 10 ⁻²	16.0	8.7	48000
5	70	2 × 10 ⁻²	1.5	9.9	54000

^a [M] = 5.0 mol l⁻¹. Solvent, toluene for run 1 and benzene for runs 2—5.

Figure 4. ¹H NMR spectra of poly(acetone divinyl acetal). a) Sample: Table III, run No. 1. 3 w/v% in C₆D₆ + *o*-C₆H₄Cl₂ at 140°C; accumulation, 64 scans. b) Sample: Table III, run No. 5. 3 w/v% in C₆D₆ + *o*-C₆H₄Cl₂ at 140°C; accumulation, 64 scans.

of 2CH₃-DVA at several temperatures. The molecular weights (8000—50000) are greater than those of the other two polymers. Figure 4

shows ¹H NMR spectra of the polymer. The following structural units are conceivable.

Spectral comparisons with the model compounds again suggest the following assignments

peak A (doublet), 1.62 ppm; 5-CH₃ proton in **XII**.

peak B (doublet), 1.82 ppm; acetal CH₃ proton in **XI** and **XII**.

peak C, 1.82 ppm; acetal CH₃ in **XIII**.

peak D, 2.13 ppm; exocyclic methylene and methine protons of all the units.

peak E, 4.14 ppm; methine proton at the 4 and 5 positions in **XIII**.

peak F, 4.50 ppm; methine proton at the 4 and 5 positions in **XI** and **XII**.

As indicated in the preceding section, the polymer spectrum is simpler at low temperatures than at high temperatures. The spectrum of a low-temperature polymer (Figure 4a) again indicates the polymer to be composed of the main structure almost exclusively. Other structural units become involved at high polymerization temperatures. The corresponding ¹³C NMR spectra are given in Figure 5. The polymer obtained at -10°C gives a simple spectrum (Figure 5a) which is consistent with the exclusive presence of structure **XI**: B (26.2 ppm), acetal CH₃; C (doublet, 26.5 ppm), exocyclic CH₂ (*meso* and *racemic* forms); D (28.9 ppm), acetal CH₃; G (doublet, 78.2 ppm), ring CH (*meso* and *racemic* forms); J (107.6 ppm), acetal C. The polymer prepared at 70°C possesses peaks assignable to structure **XII** (A, F, H and I) (Figure 5b). The presence of the *trans* ring units **XIII** and **XIV** cannot be proved definitely; however, the splitting of peak J may be ascribed to these structures.

Cyclization Process

The cyclization of the growing radicals pro-

Figure 5. ^{13}C NMR spectra of poly(acetone divinyl acetal). a) Sample: Table III, run No. 1. 15 wt% in C_6D_6 at 90°C ; accumulation, 3000 scans. b) Sample: polymer obtained in C_6D_6 at 70°C and at $[\text{M}] = 2.5 \text{ mol l}^{-1}$. 28 wt% in C_6D_6 at 75°C ; accumulation, 1500 scans.

duces either the *cis* or *trans* ring as expressed by eq 1.

The relative ease of the k_{cis} and k_{trans} processes in the case of DVF is equal to the ratio of the *cis* ring structures (I, II and V) and the *trans* ring structures (III, IV, and VI). In the ^1H NMR spectra of poly(DVF), the acetal proton peaks of structures I—VI are located at 4.5—5.0 ppm.¹¹ The peaks at 4.63 and 4.80 ppm are assigned to the *cis*-syn proton of I, II, and V and to the *cis*-anti proton of I, II, and V, respectively. The acetal protons of the *trans*

Figure 6. The relative activation energy of the *cis* and *trans* cyclizations in the polymerization of divinyl formal. Polymerization conditions: C_6H_6 solvent, $[\text{M}] = 2.5 \text{ mol l}^{-1}$.

ring are present at 4.67 ppm (structures IV and VI) and at 4.86 ppm (structure III). The ratio of the *cis* and *trans* rings are calculated from the relative peak area. The temperature dependence of the *cis*/*trans* ratio is given in Figure 6 in the form of Arrhenius plots. The difference in activation energy ($E_{cis} - E_{trans}$) determined from the slope is $-2.9 \text{ kcal mol}^{-1}$.

Similar analyses could not be conducted for poly(CH_3 -DVA) and poly(2CH_3 -DVA), since the acetal protons are not separated in their ^1H NMR spectra.

Isomerization vs. Monomer Addition

The cyclized radical either isomerizes by hydrogen abstraction or adds a monomer molecule (eq 2).

Ring stereochemistry could not be taken into consideration in this analysis, since the content of the *trans* rings is small and the respective NMR peaks are often overlapping. Thus, the results obtained are largely applicable to the *cis* ring units.

In the case of DVF polymer, the ^{13}C NMR

peak of the ring methine in structure **I** appears at 77–78 ppm and that of the methyl in structure **II** is located at 14 ppm. The terminal structure **V** can contribute to the latter peak; however, the amount of **V** is very small if at all, since the molecular weights of the polymers are 5000 to 14000.

In the case of the least isomerized poly(DVF) (Figure 1), the relative peak areas of the acetal carbon, the ring methine, and the main-chain methylene are 1 : 2.1 : 1.8. The area ratio of the ring-methine and main-chain methylene is 1.0 : 1.0 for a highly isomerized poly(DVF). The relative peak area of the ring methine and the acetal methyl is 1.8 : 1 (peaks E and B of Figure 3a) in the case of poly(CH₃-DVA), and that of the ring methine and the acetal methyl is 2.0 : 2.0 (peaks G and C of Figure 5a) in the case of poly(2CH₃-DVA). These data clearly show that the nuclear Overhauser effect is virtually the same (within $\pm 10\%$) for the CH, CH₂, and CH₃ carbons of these polymers and that the structural variation of the polymers can be discussed on the basis of the ¹³C NMR data.

Thus, the ratio of **I** and **II** in poly(DVF) is estimated very simply by comparing the heights or the areas of the methine and methyl peaks. The mole fraction of the isomerized structure, $f_m = \text{II}/(\text{I} + \text{II})$ is thus obtained. Similar estimations were performed for poly(CH₃-DVA) and poly(2CH₃-DVA). The influence of monomer concentration on f_m is given in Figure 7. In all three systems, f_m decreases with increasing monomer concentration, as anticipated from eq 2. Introduction of the methyl group at the acetal carbon lowers the extent of the isomerization.

The temperature dependence of these processes can be evaluated from the ¹³C NMR spectra of the polymers obtained at different temperatures (Tables I, II, and III). The rates of simple propagation and hydrogen migration (isomerization) are given, respectively, by

$$R_p = k_p[M \cdot]2[M] \quad (3)$$

Figure 7. Influence of monomer concentration on the mole fraction of the isomerized structures. Polymerization condition: C₆H₆ solvent, 70°C.

Figure 8. Relative activation energy of the intramolecular hydrogen abstraction and intermolecular propagation. Polymerization conditions: C₆H₆ solvent, [M] = 2.5 mol l⁻¹ for divinyl formal; C₆H₆ solvent, [M] = 5.0 mol l⁻¹ for acetaldehyde divinyl acetal and acetone divinyl acetal.

$$R_m = k_m[M \cdot] \quad (4)$$

where M· is the cyclized radical. Therefore,

$$k_p/k_m = \frac{1}{2[M]} \cdot \frac{R_p}{R_m} \quad (5)$$

Figure 8 shows Arrhenius plots for k_p/k_m . The slopes correspond to differences in the apparent activation energy between simple propagation and isomerization ($E_p - E_m$), and are always negative, being -4 kcal mol⁻¹ for DVF and CH₃-DVA and *ca.* -2 kcal mol⁻¹ for 2CH₃-DVA. Although the plots for 2CH₃-

DVA are scattered, the slope is certainly less than the others. Di-methyl substitution at the acetal carbon thus renders the k_p process energetically less favored. That is hydrogen migration is energetically less favored in the case of DVF and CH_3 -DVA. However, since the k_p/k_m values themselves are not very different among the monomers, the frequency factor is favorable for the isomerization process of the cyclized DVF and CH_3 -DVA radicals.

The conformation of 1,3-dioxolanes has been studied by Lemieux and coworkers.¹² When there is no methyl substituent at the acetal carbon, the five-membered ring assumes an eclipsed form. The *gem*-dimethyl derivative,

in contrast, assumes a skewed form. The dihedral angle of the *cis*-4,5-hydrogens is greater in the skewed form than in the eclipsed form. The distance between the exocyclic methylene radical and main chain methylene hydrogen in the *cis* cyclized radical of 2CH_3 -DVA may thus be greater than the corresponding distance in the cyclized radical of DVF. The hydrogen atom transfer would then be more favored in the DVF radical than in the 2CH_3 -DVA radical.

Reactivity of Cyclized Radicals

The relative reactivities of cyclized radical (without isomerization) **XVIII** and the subsequently isomerized radical **XIX** can be inferred from molecular weights of the polymers. The polymerizations of the three monomers were carried out at 70°C in benzene at different monomer concentrations. The relations between the initial monomer concentration and the number-average molecular weight of the polymers are illustrated in Figure 9. The slope of the double logarithmic plots is 1.2 for DVF and 1.0 for CH_3 -DVA and 2CH_3 -DVA. At this polymerization temperature (70°C), the

Figure 9. Dependence of molecular weight on monomer concentration. Polymerization conditions: C_6H_6 solvent, 70°C, $[\text{AIBN}] = 2 \times 10^{-2} \text{ mol l}^{-1}$.

intermolecular propagation occurs from both the cyclized radical **XVIII** and its isomerized derivative **XIV**. Propagation from the latter decreases with increasing monomer concentration. The observed slopes close to unity imply the reactivities of the radicals involved in the propagation to be uniform, as in typical homopolymerization. This means that the cyclized radical and isomerized radical exhibit close reactivities.

The influence of monomer concentration on the rate of cyclopolymerization has been reported. Minoura and Mitoh¹³ found the 1.5th order dependence at $[\text{M}] = 0.9\text{--}2.7 \text{ mol l}^{-1}$ and the 2.2th order dependence at $[\text{M}] = 2.7 \text{ mol l}^{-1}$ in the polymerization of DVF in benzene at 50°C. Smets *et al.*¹⁴ obtained the order of 3 in the cyclopolymerization of methacrylic anhydride. The reason why the orders are high in these cases is not clear. The microviscosity effect may be responsible in some cases. At any rate, the present systems are quite normal, and no kinetic anomaly is expected from the available data.

Concluding Remarks

The propagation scheme of divinyl acetals is given by eq 1 and eq 2. The overall rate of polymerization appears to decrease with increasing methyl substitution at the acetal carbon: $\text{DVF} > \text{CH}_3\text{-DVA} > 2\text{CH}_3\text{-DVA}$. The

polymers possess fairly uniform structures: *cis*-1,3-dioxolane rings are the major structural units, and the six-membered rings and uncyclized units are excluded. The dioxolane structural units are present in the pendent group due to radical isomerization. The formation of the pendent unit could be lowered by lowering the polymerization temperature and increasing the monomer concentration. It is thus, expected that highly regular *cis*-dioxolane polymers are obtainable in the cyclopolymerization of divinyl acetals by the proper choice of conditions.

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