trans content remains largely unchanged. As nothing is known of the relative tendencies of cis and trans active centers to form 1,2 or 1,4 in-chain units or how this varies with temperature, perhaps the only significant observation is the virtual disappearance of cis units in the chain.

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Stereochemistry and Polymerization of 1,3-Dioxolane Derivatives. VI. Reactivities of Some Stereoisomers of 2-Alkenyl-4,5-dimethyl-1,3-dioxolanes in the Cationic Polymerization by $BF_3{\cdot}Et_2O$

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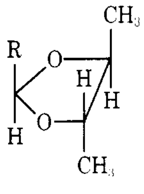
ABSTRACT: The structure–polymerization relationship for some 1,3-dioxolane derivatives was investigated. Trans and cis(syn–anti) isomers of three 2-alkenyl-4,5-dimethyl-1,3-dioxolanes were obtained and then polymerized by BF_3Et_2O in an adiabatic reactor. Polymerization rates R_p were measured. The overall rate of polymerization was found to depend on monomer configuration. For all monomers used, however, polymerization was found to be a first-order reaction with respect to the catalyst and a half-order one with respect to the monomer.

For a number of years the cationic polymerization of cyclic acetals has been a subject of considerable interest. Most of the papers deal with the polymerization and copolymerization of nonsubstituted 1,3-dioxolane, especially with its mechanism in the presence of various catalysts.[1–6] Few papers, however, have been published so far on the polymerization of dioxolane derivatives.[7–15] The polymerization of substituted acetals is a complex process, particularly in the case of acetals with unsaturated substituents for such monomers displaying a bifunctional behavior.

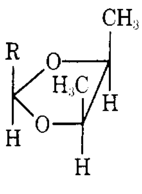
In the case of cyclic acetals containing more than one substituent in the ring stereochemical factors must be taken into account, because such compounds may occur in the form of different stereoisomers. Usually this problem has been neglected in papers dealing with the polymerization of this kind of monomers.

In the present paper the influence of the configuration of such monomers upon the rate of polymerization was taken into consideration. Some stereoisomers of 1,3-dioxolane derivatives were used as model compounds in these experiments. Three unsaturated acetals, 2-vinyl-4,5-dimethyl-1,3-dioxolane (VDMD), 2-isopropenyl-4,5-dimethyl-1,3-dioxolane (IPDMD), and 2-propenyl-4,5-dimethyl-1,3-dioxolane (PDMD), have been investigated. One can get three stereoisomers (nomenclature from Farines[16]) when synthesizing each of the acetals numbered above.

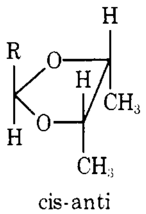
The synthesis and separation of such stereoisomers were described by us earlier[17,18] and some further information is given in the Experimental Section.



trans



cis-syn



cis-anti

Experimental Section

Materials. Acetals have been obtained by means of Fischer's azeotropic method[19] according to the procedure described in some previous publications of ours[17,18] as a result of the reaction of the reaction of *meso-* and dl-butanediol-2,3 (Suchard) with unsaturated aldehydes, acroleine, methacroleine, or croton aldehyde, in the presence of catalytic amounts of *p*-toluenesulfonic acid. In the reaction of the *dl*-butanediol-2,3 and aldehyde, the trans isomer of the corresponding acetal (fraction I) was obtained, whereas in the case of the meso diol a mixture of cis isomers, viz., cis-anti and cis-syn isomers at a ratio of about 2:3 (fraction II), was formed.

The stereoisomeric monomers were distilled over sodium and stored in phials under nitrogen. Their configuration was determined by means of NMR spectroscopy.

Some properties of the monomers were gathered in Table I. The pK_b values presented in Table I were determined by means of the spectrophotometric method.[20]

Catalyst. Boron trifluoride etherate was distilled over phosphorus pentoxide and dissolved in 1,2-dichloroethane.

Solvent. 1,2-Dichloroethane was purified by refining with sulfuric acid and distillation over phosphorus pentoxide.

Polymerization Procedure. The polymerization was carried out in an atmosphere of dry nitrogen in an adiabatic reactor,

Table I
Some Properties of the 1,3-Dioxolane Derivatives Studied

Acetal	Isomer	Boiling temp, °C (mm Hg)	$n^{25}\mathrm{D}^a$	Basicity $\mathrm{p}K_\mathrm{b}$
2-Vinyl-4,5-dimethyl-1,3-dioxolane (VDMD)	Trans	49.5 (37.5)	1.4179	8.76
	Cis (syn–anti 3:2)	55.0 (37.5)	1.4274	8.75
2-Isopropenyl-4,5-dimethyl-1,3-dioxolane (IPDMD)	Trans	59.5–60.5 (31)	1.4245	8.52
	Cis (syn–anti 3:2)	65–66 (31)	1.4317	8.00
2-Propenyl-4,5-dimethyl-1,3-dioxolane (PDMD)	Trans	55–56 (12)	1.4308	8.20
	Cis (syn–anti 3:2)	58–59 (12)	1.4360	6.41

^{a} Refractive index.

equipped with an agitator, a three-way tap, and a temperature gauge.

Fixed amounts of the solvent and of the monomer were supplied to the reactor which was connected with a thermostat; a phial ampulla with the catalyst solution ($\mathrm{BF_3{\cdot}Et_2O}$ in ethylene chloride) was inserted into the thermostat. The agitator was put into motion and the measuring system was switched on.

After the temperature had become stabilized the reactor was cut off the thermostat and a fixed amount of the catalyst solution from the thermostated phial was injected into the reactor in the nitrogen countercurrent. The temperature inside the reactor was recorded before the introduction of the catalyst as well as during the first few minutes of polymerization, when the reaction is comparatively fast until a conversion of 5 to 15% had been reached.

Measurements were repeated up to five times.

Results and Discussion

In order to calculate the fundamental kinetic equation the following simplifying assumptions have been proposed.

The effect of small temperature changes during the measurements upon the rate of polymerization is negligible.

If the reactor is fed uniformly and the concentrations of the monomer and the catalyst are rather small, the heat capacity of the system does not change.

In the first stage of the reaction the temperature increase is practically linear; the measured temperature increase is the sum of the increase brought about by the heat of reaction and the nonreactional heat (mixing, exchange, etc.).

The rate of the temperature increase caused by the nonreactional heat is constant throughout the duration of the measurements and practically equal to that recorded before the start of the reaction.

Regarding the above-mentioned assumptions, the following relations could be written:

$$R_\mathrm{p} = k[\mathrm{M0}^a[\mathrm{C}]^b \qquad (1)$$

$$R_\mathrm{p} = A\left(\frac{\Delta T_\mathrm{r}}{\Delta \mathrm{t}}\right) \qquad (2)$$

$$\frac{\Delta T_\mathrm{r}}{\Delta t} = \left(\frac{T_\mathrm{m}}{\Delta t}\right) - \left(\frac{T_0}{\Delta t}\right) \qquad (3)$$

$$A = \left(\frac{\Delta m_\mathrm{i}}{\Delta T_\mathrm{ri}}\right)\left(\frac{1}{\mu V}\right) \qquad (4)$$

where [M] and [C] are the concentrations of the monomer and of the catalyst; $\Delta T_0/\Delta t$ is the rate of the temperature increase observed before the start of the reaction; $\Delta T_\mathrm{m}/\Delta t$

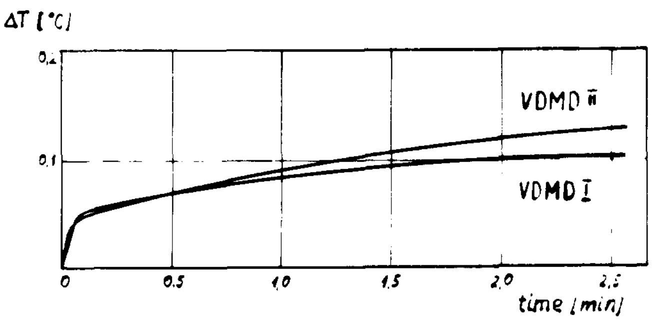


Figure 1. Time-temperature increase curves of the polymerization of the trans and cis (syn–anti) isomer: $[\mathrm{M}]_0 = 0.4$ mol l.$^{-1}$; $[\mathrm{BF_3{\cdot}Et_2O}]_0 = 20 \times 10^{-3}$ mol l.$^{-1}$; solvent $\mathrm{C_2H_4Cl_2}$; initial temp 20°C.

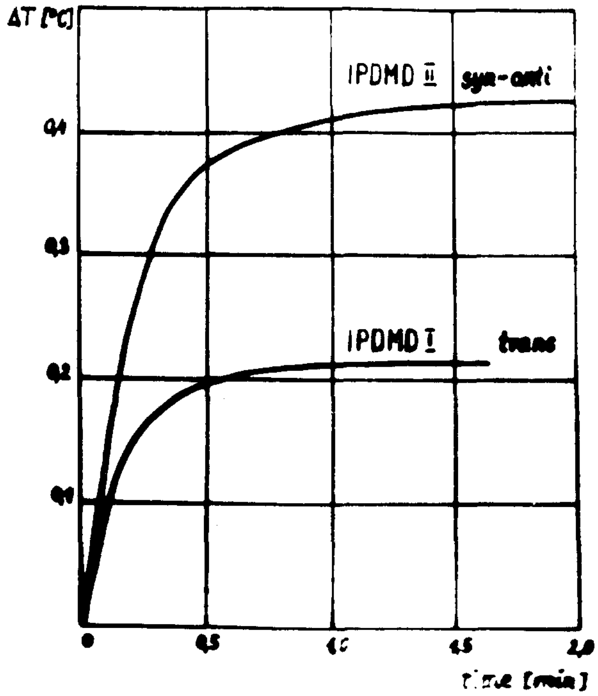


Figure 2. Same as Figure 1.

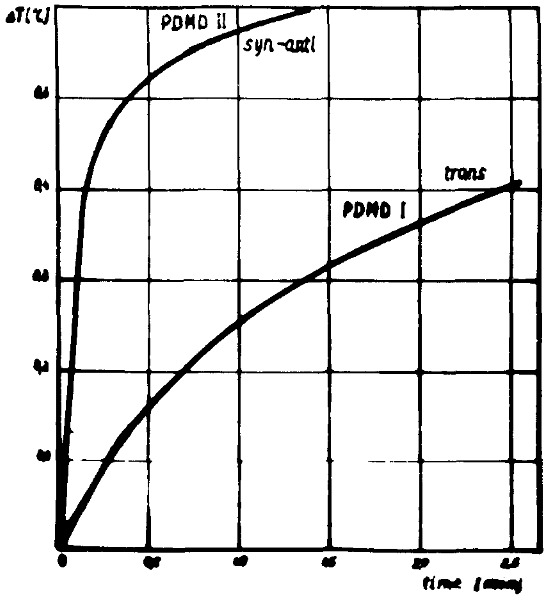


Figure 3. Same as Figure 1.

Table II
Rates of Polymerization in the Presence of $BF_3{\cdot}Et_2O$ in $C_2H_4Cl_2$ Solution ($[M] = 0.4$ mol l.$^{-1}$, $[C] = 20 \times 10^{-3}$ mol l.$^{-1}$, Temperature 20°C)

Acetal	Isomer	Rate of polymerization, mol l.$^{-1}$ min^{-1}	"a"	"b"
VDMD	Trans	0.066	0.54	1.05
	Cis(syn–anti)	0.072	0.56	1.08
IPDMD	Trans	0.096	0.55	0.87
	Cis(syn–anti)	0.112	0.52	0.89
PDMD	Trans	0.027		
	Cis(syn–anti)	0.203		

is the total rate of the temperature increase measured during the reaction; $\Delta T_r/\Delta t$ is the rate of the temperature increase, due to the heat of reaction; $\Delta m_i/T_{ri}$ is the amount of the polymerization product corresponding to some definite temperature increase effect due to the heat of reaction, which is equal, for both cis,trans isomers of particular acetals; μ is the molecular weight of the monomer; and V is the volume of the reaction mixture.

From eq 1 and 2 the following relations will result, which make it possible to calculate the order of reaction: if $[C]$ = constant

$$\log \frac{\Delta T_r}{\Delta t} = a \log [M] + D \qquad (5)$$

if $[M]$ = constant

$$\log \frac{\Delta T_r}{\Delta t} = b \log [C] + D' \qquad (6)$$

When taking into account the corrections concerning the nonreactional heat (eq 3), the rate of polymerization is proportional to the rate of the temperature increase in an adiabatic reactor. Figures 1 to 3 represent the typical shape of the temperature curves in the coordinate system temperature vs. time.

One may conclude from the shape of these curves that a characteristic feature of the polymerization of all the investigated acetals is the rapid start of the reaction without induction period. The reaction is completed in short time, depending on the type of acetals used. The ratio is fast in the first few minutes and then slows down.

The nearly linear temperature increase in the course of the first step of reaction indicates that the polymerization runs approximately in a stationary state. It may be assumed that in this step there occurs either only one of the possible reactions responsible for the growth of polymer chains, or the share occupied in the process by the numerous possible propagation reactions is constant and does not change in time.

The data contained in Table II, (e.g., 1–3) indicate that the polymerization rates of the respective monomers differ considerably.

The rate of polymerization depends not only on the kind of substituent on the C-2 atom, but also on the stereochemical configuration of given acetals.

The polymerization of the trans isomers is slower than the polymerization of isomers with a cis(syn–anti) configuration. The more the monomers differ in their nucleophilic character marked by their basicity, the greater are the differences in the polymerization rates of the stereoisomers. This observation becomes particularly distinct in the case of the polymerization of PDMD isomers.

The order of the reaction with respect to the monomer and catalyst was also determined. Values of the indices "a" and "b" in eq 1 for trans and cis(syn–anti) isomers of VDMD and IPDMD are of similar order of magnitude and this may indicate that the polymerization mechanism of different stereoisomers is similar. In the case of VDMD and IPDMD isomers the values of "a" approach 0.5, whereas the values of "b" are equal to about 1 (eq 1). This calculated order of reaction with respect to the monomer is rather untypical for the classical cationic polymerization.

Thus the propagation step does not determine the general rate of polymerization; of considerable influence is most likely some other, slower, reaction, e.g., the formation of active centers. Because of the complicated character of the polymerization process of unsaturated acetals it is difficult to determine the absolute rate constants and therefore it is risky to draw conclusions concerning the mechanism of this process on the basis of kinetic parameters obtained.

Analyses of the experimental data obtained so far show distinctly, however, that the configuration of the stereoisomer is an important factor influencing the course of the cationic polymerization of substituted cyclic acetals, run in the presence of $BF_3{\cdot}Et_2O$ as an initiator. Further investigations on this field are under way.

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