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Reversible Cationic Polymerization of Trioxepane Resulting in Establishment of Stationary Concentrations of Three Monomers. Calculation of the Stationary Concentrations and of the Frequency of Various Triads

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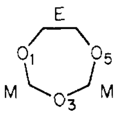
ABSTRACT: Cationic polymerization of 1,3,5-trioxepane proceeds without termination and yields living polymers. The propagation is accompanied by depropagation that prevents quantitative conversion of the monomer into polymers. Unusual complexity of this system is caused by the occurrence of alternative modes of depropagation that generate dioxolane and formaldehyde in addition to dioxepane. These act then as monomers in their own right converting the polymerization into a kind of copolymerization. Eventually, the system reaches a stationary state, and the concentrations of all three monomers then remain constant. Distinction is made between the equilibrium concentrations and stationary concentrations of the monomers. The former are determined by the free energies of the monomer and monomeric segment of regular polymers, whereas the values of the latter are proportional to the mole fractions of living polymers terminated by specific sequences of units. Treatment developed here allows the calculation of the pertinent mole fractions of polymers with specific terminal sequences of units and subsequently the stationary concentrations of the monomers as well as the frequencies of various triads in the polymer chains. The mole fractions, the stationary concentrations of the monomers, and frequencies of various triads depend on the composition of the polymers, i.e., on the ratio of $-OCH_2CH_2-$ units to $-OCH_2-$ units in the formed macromolecules.

An interesting paper describing cationic polymerization of 1,3,5-trioxepane was published recently by Schulz et al.[1] The following conclusions were derived from their observations:



1,3,5-trioxepane

(1) The investigated polymerization proceeds without termination, i.e., it yields living polymers.

(2) Both propagation and depropagation participate in the process. Consequently, the conversion of the monomer into polymers is not quantitative, and eventually its concentration reaches a stationary value when the rate of propagation is exactly balanced by the rate of depropagation.[2]

(3) The composition of the polymer differs from that of the monomer.

(4) The residual unpolymerized material is a mixture composed not only of the original monomer, trioxepane, but also of 1,3-dioxolane, which polymerizes or copolymerizes under conditions of Schulz's experiments. Dioxolane is formed in the course of polymerization, and its concentration reaches, simultaneously with trioxepane, a stationary value.

(5) Extensive NMR analysis of the polymers revealed the presence of triads such as $-OCH_2 \cdot OCH_2 \cdot OCH_2-$, denoted as –MMM–, and $-OCH_2 \cdot OC_2H_4 \cdot OCH_2-$, denoted as –MEM–.

These observations imply that two modes of trioxepane propagation are involved in the process. The $-O{=}CH_2^+$ group always is the reactive end group of these polymers, and it is denoted as $\sim\!\!\sim M^+$. The $-OCH_2CH_2^+$ group ($\sim\!\!\sim E^+$) is never formed, neither through propagation nor by depropagation. Propagation involving an attack on oxygen

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1 or 5 followed by opening of the oxonium ion yields –EMM– sequences, i.e.,

$$\sim M^+ + \text{trioxepane} \rightleftarrows \sim MEMM^+ \qquad \text{(a)}$$

whereas an attack on oxygen 3, followed by one of the two equivalent ring opening results in sequences –MEM–, i.e.,

$$\sim M^+ + \text{trioxepane} \rightleftarrows \sim MMEM^+ \qquad \text{(b)}$$

Had the propagation proceeded always by route (a) or always by route (b), the resulting polymers would be regular, i.e., $\sim$EMM·EMM·EMM····, or $\sim$MEM·MEM·MEM····. These two forms, apart from the end groups, are indistinguishable. On the other hand, addition (a) followed by (b) yields triads –MMM–, while triads –EME– are formed when addition (b) is followed by (a).

Depropagation may result in formation of alternative monomers. For example, the reaction

$$\sim M^+ + \text{trioxepane} \rightleftarrows \sim MMEM^+ \rightleftarrows \sim MM^+ + \text{dioxolane}$$

converts trioxepane into dioxolane, simultaneously yielding polymers possessing at least 2 M units on their ends. Similarly, dissociation of polymers terminated by at least 2 M units may yield CH_2O, viz.,

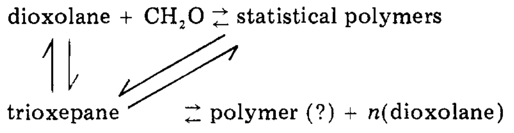
$$\sim MM^+ \rightleftarrows \sim M^+ + CH_2O$$

Since dioxolane or formaldehyde is formed in the polymerization of trioxepane, it is necessary to supplement steps (a) and (b) by steps (c) and (d)

$$\sim M^+ + \text{dioxolane} \rightleftarrows \sim MEM^+ \qquad \text{(c)}$$

$$\sim M^+ + CH_2O \rightleftarrows \sim MM^+ \qquad \text{(d)}$$

Obviously, the above system is more complex than the polymerization of most oxacyclics. Schulz et al.[1] described its course by the scheme



However, such a description does not account for the details of this process and provides no information regarding the composition of the polymers or the stationary concentrations of the monomers. We wish to show how the composition of the polymers and the stationary concentrations of the monomers can be calculated from thermodynamic data and statistical considerations.

Schulz et al.[1] refer to the stationary concentrations of the monomers as their equilibrium values. Clarification of the distinction between these two terms is desired. The equilibrium concentration of a monomer is that concentration of the monomer at which it is in equilibrium with its perfectly uniform, high-molecular-weight polymer.[2] Thus, the equilibrium concentration of trioxepane is equal to the respective equilibrium constant, K_T' or K_T'', viz.,

$$\underset{n\text{-mer}}{\sim EMM\cdot EMM\cdot EMM^+} \rightleftarrows \underset{(n-1)\text{-mer}}{\sim EMM\cdot EMM^+} + \text{trioxepane} \qquad K_T'$$

or

$$\underset{n\text{-mer}}{\sim MEM\cdot MEM\cdot MEM^+} \rightleftarrows \underset{(n-1)\text{-mer}}{\sim MEM\cdot MEM^+} + \text{trioxepane} \qquad K_T''$$

At this stage, we allow for distinction between K_T' and K_T'', but it will be shown later that $K_T' = K_T''$. In an analogous way, the equilibrium concentrations of dioxolane and of CH_2O, in contact with their living, uniform, high-molecular-weight polymers, are given by the equilibrium constants, K_D and K_F, respectively, i.e.,

$$\underset{n\text{-mer}}{\sim EM\cdot EM\cdot EM^+} \rightleftarrows \underset{(n-1)\text{-mer}}{\sim EM\cdot EM^+} + \text{dioxolane} \qquad K_D$$

and

$$\underset{n\text{-mer}}{\sim MMM^+} \rightleftarrows \underset{(n-1)\text{-mer}}{\sim MM^+} + CH_2O \qquad K_F$$

These equilibrium constants, and therefore the monomer equilibrium concentrations, are independent of the mechanism of polymerization[2] and uniquely determined by the free energy of the monomer and of the monomeric segment of the respective uniform, high-molecular-weight polymer.

The situation is more complex in the system under discussion. In systems restricted to a single kind of uniform polymer, every living macromolecule can add its monomer as well as depropagate into its monomer. In the present system, every living macromolecule may still add any one of the three monomers, trioxepane, dioxolane, or CH_2O; however, only a *fraction* of the living macromolecules may depropagate into a specific monomer. In particular, polymers terminated by a sequence $\sim MEMM^+$ can dissociate into trioxepane or CH_2O but not into dioxolane, and those terminated by $\sim MMEM^+$ could form on dissociation trioxepane or dioxolane but not CH_2O. Polymers terminated by $\sim MMM^+$ dissociate only into CH_2O, while those terminated by $\sim EMEM^+$ yield on dissociation only dioxolane.

In what follows we assume that the rates of propagation depend only on the nature of the added monomer, while the rate of depropagation in which monomer X is expelled and a new $\sim M^+$ left, viz.,

$$\sim MX^+ \rightleftarrows \sim M^+ + X$$

depends only on X and not on the nature of units preceding the $\sim M^+$ to be formed. For example, $\sim EM^+$ and $\sim MM^+$ are equally reactive in any addition, and $\sim EMM^+$ and $\sim MMM^+$ dissociate with equal rate constants into CH_2O. Let us denote by f_{MEMM^+}, f_{MMEM^+}, f_{MEM^+} and f_{MM^+} the mole fractions of polymers terminated by $\sim MEMM^+$, $\sim MMEM^+$, $\sim MEM^+$, and $\sim MM^+$, respectively. These mole fractions become constant when the system attains its stationary state. Of course, $f_{MEM^+} + f_{MM^+} = 1$, while $f_{MEMM^+} < f_{MM^+}$ and $f_{MMEM^+} < f_{MEM^+}$.

At the same concentration of living polymers, the pseudo-first-order rate constant of a monomer addition is the same whether the polymers are uniform or not. However, the rate of their dissociation into that monomer is smaller in the system studied here than in those involving uniform polymers because in the former case only a fraction of the living polymers is capable of dissociating into that monomer. Therefore, the stationary concentrations are given by the equilibrium concentrations multiplied by the respective mole fractions, viz.,

$$[\text{trioxepane}]_{st} = K_T' f_{MEMM^+} = K_T'' f_{MMEM^+}$$

$$[\text{dioxolane}]_{st} = K_D f_{MEM^+}$$

$$[CH_2O]_{st} = K_F f_{MM^+}$$

Let us idealize the system by assuming identical composition of all the macromolecules and high molecular weight for all polymers, although their molecular weight distribution may be arbitrary. By the composition we understand the ratio of E units to M units in the polymers, here denoted by r. Enthalpy of a polymer terminated by M^+ and composed of n E units and m M units (excluding the terminal M^+) is unaffected by any permutation of the segments subject to the obvious condition that no two E's are adjoined.[3] This follows from the fact that such permutations leave invariant the number of M–M and E–M (or M–E) bonds. The condition of disjoined E's is automatically fulfilled if one permutes EM units and the remaining M units. Hence, the number of allowed permutations of E's and M's that leave E's disjoined is given by the sum of the total number of permutations of n EM's and $(m - n)$ M's (M preceding $-M^+$) and the total number of permutations of $(n - 1)$ EM's and $(m - n + 1)$ M's (E preceding $-M^+$), viz., $(m + 1)!/n!(m - n + 1)!$. In a similar way, one finds the number of allowed permutations in polymers terminated by $-MM^+$ to be $m!/n!(m - n)!$, in polymers terminated by $-MEM^+$ to be $m!/(n - 1)!(m - n + 1)!$, and in polymers terminated by $-MEMM^+$, or $-MMEM^+$, to be $(m - 1)!/(n - 1)!(m - n)!$. Since the probabilities of finding macromolecules corresponding to each permutation are the same, one finds the mole fractions of polymers terminated by $-MM^+$, $-MEM^+$, $-MEMM^+$, and $-MMEM^+$ to be

$$f_{MM^+} = (m - n + 1)/(m + 1) \approx 1 - n/m = 1 - r$$

$$f_{MEM^+} = n/(m + 1) \approx n/m = r$$

$$f_{MEMM^+} = f_{MMEM^+} = n(m - n + 1)/m(m + 1) \approx (n/m)(1 - n/m) = r(1 - r)$$

These approximations are justified because m and n are very large.

To simplify the above derivation, let it be stressed that the polymers may be treated as random sequences of ME's and residual M's present in the ratio $r{:}(1 - r)$, provided that $\gamma = 1$. The probabilities that a site along such a chain is ME or residual M are then r and $(1 - r)$, respectively. Hence mole fractions $f_{MM^+} = (1 - r)$ and $f_{MEM^+} = r$, since these are the probabilities that the penultimate site is a residual M or an ME. Likewise, $f_{MEMM^+} = f_{MMEM^+} = r(1 - r)$. The last equation, combined with the previously mentioned equality, $K_T' f_{MEMM^+} = K_T'' f_{MMEM^+}$, shows $K_T' = K_T'' = K_T$.

We found now the stationary concentrations of the monomers in contact with the polymers having composition r, namely

$$[\text{trioxepane}]_{st} = K_T r(1 - r)$$

$$[\text{dioxolane}]_{st} = K_D r$$

$$[CH_2O]_{st} = K_F(1 - r)$$

Note that the stationary concentrations of the monomer depend on the composition of the polymer and therefore on the composition and *concentration* of the initial feed. For example, say the polymerization was initiated in trioxepane solution of initial concentration C_0. Then the stoichiometric balance requires

$$\{C_0 - K_T r(1 - r) - K_D r\}/\{2C_0 - 2K_T r(1 - r) - K_D r - K_F(1 - r)\} = r$$

i.e., r is determined by C_0.[4]

The treatment outlined here provides us with a method of calculating the frequency of occurrence of at least three consecutive M's, viz., $(1 - r)^2/(1 + r)$, and of two E's separated by one M, viz., $r^2/(1 + r)$. Likewise, the frequency of MEM's, like the frequency of E's, is $r/(1 + r)$, while the frequencies of EMM's or MME's are $r(1 - r)/(1 + r)$.

Finally, the approach used here applies also to high molecular weight polymers of nonuniform composition provided that the average value of $\langle r \rangle$ is substituted for a definite r.

The equilibrium, trioxepane $\rightleftarrows$ dioxolane + CH_2O (K_a) has to be maintained in the stationary state. Hence

$$K_a K_T = K_D K_F$$

Approximate calculation gives $K_a \approx 10^{-3}$ M. Thus for $[\text{trioxepane}]_{st} = 0.8$ M and $[\text{dioxolane}]_{st} = 0.5$ M the $[CH_2O]_{st} \approx 10^{-3}$ M.

Our approach exhibits the distinction between equilibrium and stationary-state concentrations. Whereas the equilibrium concentrations are uniquely determined by the thermodynamics, the stationary-state concentrations depend on r, the composition of the polymer, and therefore on the initial concentrations of the monomers. Schulz et al.[1] plotted ln $[\text{trioxepane}]_{st}$ vs. $1/T$ and obtained "apparent" $\Delta S_{ss} = -18.9$ J/(mol deg) and $\Delta H_{ss} = -6.6$ kJ/mol. With the same data, a plot of ln $([\text{trioxepane}]_{st}/r(1 - r))$ vs. $1/T$ gives the thermodynamic entropy and enthalpy for polymerization of trioxepane to uniform polymer,[6] viz.,

$$\Delta S = -31.5 \text{ J/(mol deg)}$$

$$\Delta H = -6.9 \text{ kJ/mol}$$

These values agree better with the corresponding values, −38.9 J/(mol deg) and −13.4 kJ/mol, for polymerization of 1,3-dioxepane,[5] the closest model which produces uniform polymer. The "apparent" entropy of polymerization is less negative than the thermodynamic entropy because of the randomization of M and ME units. Likewise, from the data of Schulz et al.[1] a plot of ln $([\text{dioxolane}]_{st}/r)$ vs. $1/T$ gives entropy and enthalpy for polymerization of dioxolane, namely,

$$\Delta S = -83 \text{ J/(mol deg)}$$

$$\Delta H = -24.4 \text{ kJ/mol}$$

which may be compared with values −59 J/(mol deg) and −15 kJ/mol, respectively, previously found.[5]

Addendum

In reply to a referee's comment, we wish to point out that transfer of the growing polymer end to –O– of the same or another chain speeds up the equilibration of the various possible end groups discussed in our paper. However, such a transfer does not produce any of the three monomers and therfore this reaction need not be considered when one calculates the stationary concentrations of the three monomer or the stationary frequencies of various triads in the polymer chains.

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References and Notes

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(2) M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes", Wiley-Interscience, New York 1968, pp 104–148.

(3) The small difference in strength of $-M-M^+$ and $-E-M^+$ bonds leads to a small change of enthalpy of molecules terminated by $-M{\cdot}M^+$ and $-E{\cdot}M^+$. The respective Boltzmann factor is denoted by γ. However, in what follows we assume $\gamma = 1$.

(4) The above equation may be generalized for other feeds, e.g., mixtures of trioxepane and dioxolane. However, the ratio of M/E units in the feed must be greater than 1.

(5) Y. Yamashita et al., *Makromol. Chem.*, **114**, 146 (1948).

(6) r is calculated from the equation $\{5 - [\text{trioxepane}] - [\text{dioxolane}]_{st}\}/\{10 - 2[\text{trioxepane}]_{st} - [\text{dioxolane}]_{st}\} = r$ using Schulz's data and taking $[CH_2O]_{st} \approx 0$.