populations ($N = 4$), it would be advantageous to increase the data base, e.g., by compounding the batches. Figure 3 illustrates these results when $(1 - X)$ is computed for each batch/dose combination (cf. Table I). The regression plot for this case (solid line) has a slope which equals 18.3 $\times 10^{-4}$ such that $G$(-units) = 18.3 (eq 2a). Discarding the wild point at (-0.08, 72) yields $G$(-units) = 14.8 for an $r = 0.91$ and a $P = 0.01$ (Table II).

These experiments indicate that $G$(-units) $\approx 15$, in good agreement with a cryoscopic technique[7,8] in which $G$(-units) = 12 (cf. dashed line, Figure 3). Both $G$ values differ from $G$(fractures) = 1.7, obtained either by gas analysis[14] or by molecular weight measurements.[4,5,7,15] The present viewpoint is that both sets of results are correct, the former measuring both the chemical and physical damage while the latter measuring only chemical changes. In the case of isotactic PMMA, the difference in $G$(-units) is attributed to physical damage associated with radiation-induced racemization.[15] Thus the present case graphically shows that significant damage can result in the solid state, which by more established methods might otherwise go undetected. These preliminary X-ray data verify the magnitude of that damage.

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# Some Comments on the Kinetics of Cationic Polymerization of Tetrahydrofuran

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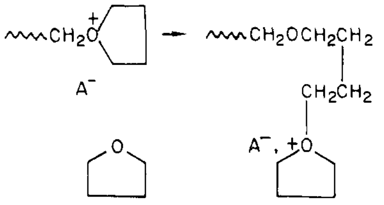
The kinetics of cationic polymerization of tetrahydrofuran was studied by numerous workers[1-10] in the bulk and in various solvents. The polymerization is reversible, and under proper conditions its termination may be avoided, at least within the period of the experiments. Hence, the resulting polymers are living and the system tetrahydrofuran-(monomer THF) living poly(tetrahydrofuran) attains a state of equilibrium when the concentration of the monomer reaches the equilibrium value $[THF]_e$ that depends on temperature and the composition of the system.

For a rapid and quantitative initiation only the propagation contributes to the monomer's consumption at later stages of polymerization. Indeed, all the investigators found the rate of the reaction, $-d[THF]_t/dt$ to be given by $k_pI_0\{[THF]_t - [THF]_e\}$, at that stage of the process, where $k_p$ is the bimolecular propagation constant, $I_0$ denotes the initial concentration of the initiator eventually quantitatively converted into living polymers, and $[THF]_t$ and $[THF]_e$ are the monomer concentrations at time $t$ and at its equilibrium with the polymer, respectively.

None of the students of THF polymerization commented on this simple relation $-d[THF]_t/dt = k_pI_0([THF]_t - [THF]_e)$. It appeared obvious. The problem of how $k_p$ is affected by the composition of the reacting mixture was dealt with by some investigators, notably by Penczek's group.[11] They found the propagation constant of the oxonium pairs, i.e., $k_{p\pm}$ briefly denoted by $k_p$, to *decrease* with *increasing initial* concentration of THF in the mixture of carbon tetrachloride and the monomer and attributed this result to change of the bulk dielectric constant of the medium. In fact, a linear relation was claimed for ln $k_{p,\pm}$ with the reciprocal of bulk dielectric constant. The seemingly obvious relation $-d[THF]_t/dt = k_pI_0([THF]_t - [THF]_e)$ and the dependence of $k_p$ on the composition of the medium calls for comments, and I wish to examine closer this subject in this note. The composition of the medium may affect the ratio of ion pairs to macroesters and thus the overall $k_p$. However, I will be concerned here only with the variation of $k_{p\pm}$, the rate of propagation due to oxonium counterion pairs.

Cationic polymerization of THF is propagated by the oxonium ion pairs. (The following discussion applies to propagation by oxonium ion pairs and not by macroesters.) The composition of the medium around the ionic pairs is, on the whole, different from its nominal composition. The fact that the relation $-d[THF]_t/dt \sim ([THF]_t - [THF]_e)$ applies to the polymerization initiated in pure tetrahydrofuran suggests that the solvating power of a THF molecule is comparable to the solvation power of a monomeric segment of poly(tetrahydrofuran). Only then is the probability of finding oxygen atoms of THF molecules neighboring an oxonium ion given by the volume fraction of THF in the monomer-polymer mixture, or approximately by its mole fraction, $\alpha = [THF]_t/[THF]_{bulk,0}$.[12]



Addition of a neighboring THF molecule to a growing oxonium ion is the rate-determining step of propagation. In bulk polymerization this forward process is governed by a unimolecular rate constant $k_u$ multiplied by $\alpha$. The replacement of the added THF molecule by another one arriving from the interior of the solution is diffusion controlled and therefore it does not affect the rate of the forward reaction. In these terms one gets for bulk polymerization of THF the relation

$$-d[THF]_t/dt = k_u(\alpha - \alpha_e)I_0$$

where $\alpha_e = [THF]_e/[THF]_{bulk,0}$.

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When a THF–polymer mixture is diluted by a poorly solvating agent, say carbon tetrachloride, the immediate surroundings of the oxonium ion remain virtually unaltered, or only slightly modified. Therefore, for the same fraction $\alpha' = \alpha$ of monomer not converted to polymer, the rate of polymerization is approximately the same after dilution as it was in bulk polymerization, i.e.

$$-\mathrm{d}[\mathrm{THF}]_t/\mathrm{d}t = k_\mathrm{u}(\alpha' - \alpha_\mathrm{e}')I_0$$

where $\alpha'$ and $\alpha_\mathrm{e}'$ are the ratios $[\mathrm{THF}]_t/[\mathrm{THF}]_0$ and $[\mathrm{THF}]_\mathrm{e}/[\mathrm{THF}]_0$, respectively, and $[\mathrm{THF}]_0$ is the initial concentration of THF after dilution.

The kinetic data are always reported in terms of calculated *bimolecular* rate constant, $k_\mathrm{p}$, of propagation, i.e.

$$-\mathrm{d}[\mathrm{THF}]_t/\mathrm{d}t = k_\mathrm{p}(\alpha' - \alpha_\mathrm{e}')[\mathrm{THF}]_0I_0$$

and, hence, $k_\mathrm{u} = k_\mathrm{p}[\mathrm{THF}]_0$ or $k_\mathrm{p} = k_\mathrm{u}/[\mathrm{THF}]_0$. Since $k_\mathrm{u}$ is independent of the initial monomer concentration, the treatment outlined here, and not the variation of bulk dielectric constant of the medium, accounts for the findings of Penczek's group, i.e., for increasing $k_\mathrm{p}$ on dilution of the polymerizing medium by an oxonium ion nonsolvating diluent. Indeed, the bulk dielectric constant of the medium should be of little significance in determining the propagation constant of polymerization performed under these conditions.

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(12) The probability of finding THF around the oxonium ion is proportional to $\alpha$ and to the preferential solvating power of THF, $\beta$, as compared with the solvating power of a monomeric segment of poly-THF, $(1 - \beta)$. Thus the fraction of THF molecules in the solvating shell is given by $\alpha\beta/\{\alpha\beta + (1 - \alpha)(1 - \beta)\}$. This expression is reduced to $\alpha$ for $\beta = {}^1/_2$ and to 1 for $(1 - \beta) = 0$. The first-order relation $-\mathrm{d}[\mathrm{THF}]_t/dt \sim [\mathrm{THF}]_t - [\mathrm{THF}]_\mathrm{e}$ requires $\beta \approx {}^1/_2$. For $\beta \approx 1$, i.e., when the solvating power of THF greatly exceeds that of a monomeric segment of poly-THF, the propagation should be governed by zero-order kinetics.

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# Configurational Properties of Flexible Polymer Chains

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The theoretical study of simple polymer chain configurations by restricting each internal rotational angle to a finite number of possible values (e.g., either a trans, gauche plus, or gauche minus configuration[1]) is useful because it facilitates the rapid calculation of many chain properties. The details of this approach have been well developed by Flory.[2] Little attention has been given to the effect of this restriction on the results obtained, largely because of the difficulty of incorporating a continuous internal rotational angle potential into a tractable theory and also due to the apparent success of the Flory formalism. However, rotational angle flexibility, and the resulting enhanced flexibility of the chain, may be important features to include in the study of certain problems. Dielectric relaxation studies on macromolecules are frequently aimed at a study of the relaxation motions of short segments of chains. In order to explain the relaxation modes for certain polymers, internal rotations must be theorized, which in the strict three-state model require passage over energy barriers.[3] If some play in the internal rotational angles is allowed, then there will be a contribution to the dynamic properties which does not require passage over a barrier, and so the apparent barrier deduced from an Arrhenius plot would be lower than the real one. In another area the rate of intrachain fluorescence quenching for reasonably small chains (10–20 bonds) with fluorescent and quenching moieties on opposite ends[4] can be modeled by looking for those configurations which bring the ends of the chain within a certain distance. Preliminary studies of this problem strongly suggest that internal rotational angle flexibility may be essential to a successful theory, since it allows for quenching in situations where the three-state configuration would not.[5]

These problems and others suggest that a careful study of the effect of internal rotational angle flexibility would be valuable. In this note, some preliminary results are presented which indicate that, even for short chains, the distribution of end-to-end distances for a *single* configuration is considerable when small deviations are allowed in the internal rotational angles. A configuration c of a model $n$-bond polymethylene chain is defined by selecting the $n - 2$ internal rotational angles $\{\phi_i\}_\mathrm{c}$ to be either trans, gauche plus, or gauche minus. The end-to-end distance, $r_\mathrm{c}$, is then calculated using unit bond lengths and 112° bond angles. In order to model a flexible chain, the internal rotational angles are modified by adding a deviation to each. The deviations are picked by a Monte Carlo method such that the probability of a given deviation is given by

$$P(\Delta\phi_i) = \frac{1}{a(2\pi)^{1/2}} \exp(-{}^1\!/_2(\Delta\phi_i)^2/a^2) \qquad (1)$$

where $\Delta\phi_i$ is the deviation (both positive and negative values are possible) to be added to $\phi_i$, and $a$ is the root mean square deviation, which is picked to determine the degree of flexibility. Values of $a$ in the range of 10 to 20° correspond to what one would infer from the bond rotational energy function. This gives a new set, $\{\phi_i^\mathrm{f}\}_\mathrm{c}$, of rotational angles, and also a new end-to-end distance $r_\mathrm{c}^\mathrm{f}$. The process is repeated many times (25 000 for the data presented here) to give a set of flexible chain end-to-end distances which describe a distribution function $F(r_\mathrm{c}^\mathrm{f})$. In reporting the preliminary results of this study focus will be placed on the breadth of the distribution $F(r_\mathrm{c}^\mathrm{f})$ as a function of (1) the rigid three-state end-to-end distance and (2) the root mean square deviation parameter $a$.

In Figure 1 the $F(r_\mathrm{c}^\mathrm{f})$ for three ten-bond configurations with different rigid end-to-end distances are plotted. In each case the root mean square deviation, $a$, is taken as 10°. These particular configurations were chosen as being

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