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Distribution of Cyclic and Linear Macromolecules in the Polymerization of Cyclic Monomers with Simultaneous Backbiting and End biting Reactions

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Distribution of Cyclic and Linear Macromolecules in the Polymerization of Cyclic Monomers with Simultaneous Backbiting and Endbiting Reactions

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ABSTRACT

A system is discussed in which two kinds of cyclic macromolecules, without and with the active center located on the ring, are formed from linear ones (and vice versa) by two discrete processes: backbiting and endbiting, respectively. Thus, the probability of cyclization is not a function of the distance between one kind of the reacting groups, as in the Jacobson-Stockmayer (J-S) theory, but there are two sets of groups that can react and lead to cyclization. The proportion of the end-to-end process in the linear $\rightleftharpoons$ cyclic macromolecule equilibration decreases with an increase in the average degree of polymerization of the macromolecules, as was assumed, but it differs from the J-S theory. The present treatment gives a quantitative solution of this new system; equations describing the equilibrium distribution of cyclic and linear oligomers are formulated. These equations are solved numerically, and the dependence of the fraction of macrocyclics, the dependence of the number-average degrees of polymerization of the linear and cyclic macromolecules on the initial monomer and initiator concentrations, and the dependence on the equilibrium constant of endbiting are determined.

INTRODUCTION

Previous studies of macrocyclization have generally been limited to the polymerization conditions at which the average degree of polymerization of a linear polymer was much higher than that of cyclic oligomers. The nature of the terminal groups could thus be neglected. A detailed review on the ring-chain equilibria has recently been published by Semlyen [1].

However, there are also reports indicating the dependence of the fraction of macrocycles on the chemical structure of the endgroups (determined by the nature of the initiator). These observations have been made in the cationic polymerization of cyclic acetals and THF [2, 3].

In the polymerization of cyclic acetals or THF initiated with protonic acids (e.g., CF_3SO_3H), hydroxyl endgroups, susceptible to the attack of the cationic active centers, are formed. Thus, macrocyclic oligomers are produced not only in the backbiting reactions but also in the reversible reaction between endgroups of the living macromolecule. For example:

$$(1)$$
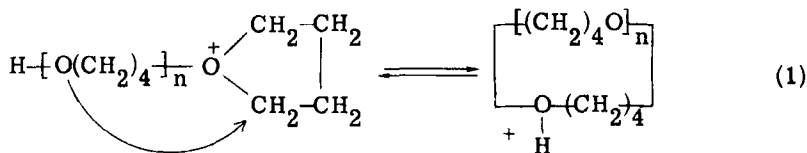
In this reaction, macrocycles with "active center on the ring" (protonated) are formed.

The initiation of THF polymerization with $CF_3SO_3CH_3$ leads to macromolecules with $CH_3O(CH_2)_4-\cdots$ endgroups. The $CH_3O(CH_2)_4-$ $\cdots$ endgroups are much less reactive toward the oxonium active centers than the hydroxyl endgroups, and thus do not participate in end-to-end cyclization.

In the case of macromolecules with endgroups that readily react with active centers, end-to-end cyclization can contribute significantly to the total fraction of cyclic oligomers.

Indeed, we have shown that for short chains the fast ring closure reactions between active centers and the endgroups can lead to concentrations of macrocycles higher than those which are established when the whole set of reactions constituting the propagation process reaches equilibrium (kinetic enhancement in macrocycles) [4]. In this work a system with parallel backbiting and endbiting reactions is analyzed with the purpose of disclosing the influence of formation of cyclic oligomers with active centers on the ring on the equilibrium distribution of macrocycles.

RESULTS AND DISCUSSION

Distribution of the Cyclic and Linear Oligomers in the Polymerization with Simultaneous Backbiting and Endbiting Reactions—Extension of the Jacobson-Stockmayer (J-S) Theory on Systems with End-to-End Cyclization

Equations describing the distribution of cyclic and linear oligomers were obtained by applying the principle of microreversibility to the system with reaction steps responsible for macrocyclization. Denoting cyclic oligomers with m monomer units as M_m, cyclic oligomers with n monomer units bearing an active center as C_n, and linear macromolecules constituted of n (or n + m) monomer units as L_n (or L_{n+m}), one can write the polymerization scheme with simultaneous cyclization. In this scheme the reversible propagation with participation of macrocycles and the reversible endbiting reactions are taken into account:

$$L_n + M_m \xrightleftharpoons{K_{p(m)}} L_{n+m}$$

$$L_n \xrightleftharpoons{K_{e(n)}} C_n \tag{2}$$
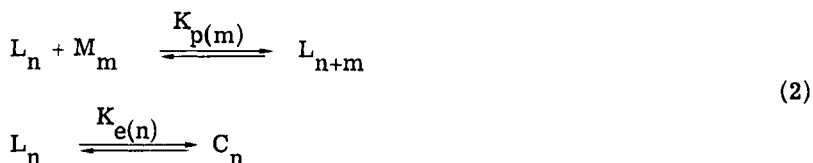
$K_{p(m)}$ and $K_{e(n)}$ are the propagation and endbiting equilibrium constants, dependent (indexes m and n) on the respective degrees of polymerization of the macromolecules involved. The equilibrium between two kinds of cyclics ($C_n + M_m \rightleftharpoons M_n + C_m$) has not been included in Scheme (2) because, due to the principle of microreversibility, its position is determined by the equilibria of propagation and endbiting.

The above scheme differs from that on which the J-S theory is based [5] by the addition of the endbiting reactions. The distribution of the cyclic and linear macromolecules involved in Reactions (2) can be found from the corresponding equilibrium equations when the sets of $K_{p(m)}$ and $K_{e(n)}$ values are known.

For the sake of simplicity, we now assume that the conformations of the chain macromolecules are governed by Gaussian statistics. This is true for macromolecules in θ solvents, with no energetic restrictions imposed on conformers in the cyclic conformations [6].

As shown in the Appendix, in the case of the chains obeying Gaussian statistics, the distribution of macromolecules resulting from Scheme (2) can be described by

$$[L_n] = \{[I]_0/[K_{e(1)}\Phi(q,3/2) + q/(1-q)]\} q^n \tag{3}$$

$$[M_n] = (1/K_{p(1)})q^n/n^{5/2} \tag{4}$$

$$[C_n] = \{[I]_0 K_{e(1)}/[K_{e(1)}\Phi(q,3/2) + q/(1-q)]\} q^n/n^{3/2} \tag{5}$$

where $[L_n]$, $[M_n]$, and $[C_n]$ denote the equilibrium concentrations of the linear macromolecules and of the two kinds of macrocycles, respectively; $[I]_0$ is used for the initial concentration of initiator; $q = K_{p(1)}[M_1]$; and $\Phi(q,3/2) = \sum_{n=1}^{\infty} q^n/n^{3/2}$. Jacobson and Stockmayer defined the function $\Phi(q,s)$ as $\Phi(q,s) = \sum_{n=1}^{\infty} q^n/n^s$ [5], and the values of this function can be calculated by using the method worked out by Truesdell [7].

It is convenient to express the concentrations of all species in $1/K_{p(1)}$ units. In these units the concentrations of the corresponding compounds are defined in the following way: $[m_n] = K_{p(1)}[M_n]$, $[c_n] = K_{p(1)}[C_n]$, $[l_n] = K_{p(1)}[L_n]$, and $[i]_0 = K_{p(1)}[I]_0$ will be dimensionless, and Eqs. (3)-(5) will be

$$[l_n] = \{[i]_0/[K_{e(1)}\Phi(q,3/2) + q/(1-q)]\} q^n \tag{6}$$

$$[m_n] = q^n/n^{5/2} \tag{7}$$

$$[c_n] = \{[i]_0 K_{e(1)}/[K_{e(1)}\Phi(q,3/2) + q/(1-q)]\} a^n/n^{3/2} \tag{8}$$

Equations (6)-(8) can be used to determine the distribution of linear and cyclic macromolecules for chosen initial monomer and initiator concentrations and for a chosen $K_{e(1)}$, provided the value of the parameter q is known. The value of q can be found from the equation corresponding to the requirement that the total concentration of monomer units in all linear and cyclic molecules is equal to the initial monomer concentration.

Indeed, let us denote the concentrations l', m', and c' of the monomeric units incorporated into the linear and cyclic macromolecules as: $l' = \sum_{n=1}^{\infty} n[l_n]$, $m' = \sum_{n=1}^{\infty} n[m_n]$, and $c' = \sum_{n=1}^{\infty} n[c_n]$. Remembering that $\sum_{n=1}^{\infty} nq^n = q/(1-q)^2$, $\sum_{n=1}^{\infty} q^n/n^s = \Phi(q,s)$, and using Expressions (6)-(8) for $[l_n]$, $[m_n]$, and $[c_n]$, we obtain, after summation,

$$l' = [i]_0 q / \{ [K_{e(1)} \Phi(q, 3/2)(1-q) + q] \, (1-q) \} \qquad (9)$$

$$m' = \Phi(q, 3/2) \qquad (10)$$

$$c' = [i]_0 K_{e(1)} \Phi(q, 1/2) / [K_{e(1)} \Phi(q, 3/2) + q/(1-q)] \qquad (11)$$

The equation corresponding to the requirement that the total concentration of the monomer units incorporated into the linear and cyclic molecules equals the initial monomer concentration $[m_1]_0$ is

$$[m_1]_0 = l' + m' + c' \qquad (12)$$

where l', m', and c' are determined by Formulas (9)–(11). The value of the parameter q can be found by solving Eq. (12) numerically with the known values of $K_{e(1)}$, $[i]_0$, and $[m_1]_0$, and thereafter the concentrations of the linear and cyclic oligomers can be calculated by using Eqs. (6)–(8).

Equations (6)–(8) can also be used to obtain the formulas for the total concentrations of the linear and the corresponding cyclic macromolecules: $l_t = \sum_{n=1}^{\infty} [l_n]$, $m_t = \sum_{n=1}^{\infty} [m_n]$, $c_t = \sum_{n=1}^{\infty} [c_n]$. After the summations are performed in a similar way as previously, one obtains

$$l_t = [i]_0 q / [K_{e(1)} \Phi(q, 3/2)(1-q) + q] \qquad (13)$$

$$m_t = \Phi(q, 5/2) \qquad (14)$$

$$c_t = [i]_0 K_{e(1)} \Phi(q, 3/2) / [K_{e(1)} \Phi(q, 3/2) + q/(1-q)] \qquad (15)$$

Comparison of Eqs. (6)–(8), describing the distribution of linear and cyclic oligomers, with the corresponding equations obtained by Jacobson and Stockmayer [5], shows that the dependencies of $[l_n]$ and $[m_n]$ on n are of the same character ($[l_n] \sim q^n$, $[m_n] \sim q^n/n^{5/2}$) regardless of the presence of endbiting. However, in the system with endbiting the coefficient in the equation describing the distribution of linear macromolecules (Eq. 6) depends on $K_{e(1)}$ (the equilibrium constant of endbiting of the monomeric chain). Of course, in the system with $K_{e(1)} = 0$, i.e., without endbiting, Eqs. (6)–(8) yield $[c_n] = 0$, and the distributions of cyclic and linear oligomers are the same as in the J–S theory.

Fraction of Macrocycles, Number-Average Degree
of Polymerization of Macrocycles, and of Linear
Macromolecules as a Function of the Initial
Monomer and Initiator Concentrations and of the
Equilibrium Constant of Endbiting $(K_{e(1)})$

The aim of this work, besides the formulation of equations de-
scribing the distribution and the total concentrations of linear and
cyclic oligomers (Eqs. 6-8 and 13-15, respectively) as well as the
formulation of equations for the concentrations of monomer units in
linear macromolecules and in cyclics (Eqs. 9-11), was to calculate
the values of several observable parameters for different initial mono-
mer and initiator concentrations and for different efficiencies of end-
biting (different values of $K_{e(1)}$). The values of the following param-
eters have been calculated (by determining q from Eq. 12 and by using
Formulas 9-11 and 13-15):

$f_{m,c} = (m' + c')/[m_1]_0$ the proportion of monomer in-
corporated into macrocycles

$\bar{D}(m) = m'/m_t$ the number-average degree of
polymerization of neutral macro-
cycles

$\bar{D}(c) = c'/c_t$ the number-average degree of
polymerization of macrocycles
with active centers

$\bar{D}(m,c) = (m' + c')/m_t + c_t)$ the number-average degree of
polymerization of the total
fraction of macrocycles

$\bar{D}(l) = l'/l_t$ the number-average degree of
polymerization of linear macro-
molecules

The calculations were performed with initiator and monomer con-
centrations which varied from 10^{-4} to 1 and from 1.5 to 10, respec-
tively, and for values of $K_{e(1)}$ ranging from 10^{-2} to 10^6.

The lowest value of $K_{e(1)}$ used in the calculations, equal to 10^{-2},
corresponds to the system with practically insignificant endbiting and
with the majority of macromolecules with active centers present in
the form of linear ones. On the other hand, the results obtained by
using $K_{e(1)} = 10^6$ describe the other extreme case, in which among
the low molecular weight oligomers with active centers the fractions
of linear ones are negligible. Indeed, it follows from Eqs. (6) and (8)
that the proportion of macromolecules with active centers and with a

given degree of polymerization (n) present in the system as linear ones equals

$$[l_n]/([l_n] + [c_n]) = n^{3/2}/(K_{e(1)} + n^{3/2}) \tag{16}$$

Thus, for instance, when $K_{e(1)} = 10^{-2}$ the proportions of linear macromolecules in the sets of macromolecules with active centers and with degrees of polymerization DP = n = 1, 2, 3, and 4 equals 99.01, 99.65, 99.81, and 99.88%, respectively. Therefore the remaining fractions of cyclic oligomers with active centers are negligible and the system with $K_{e(1)} = 10^{-2}$ does not differ significantly from the system analyzed in the J-S theory [5]. On the contrary, when $K_{e(1)} = 10^6$, the fractions of linear oligomers with active centers are negligible; e.g., for DP = 1, 2, 3, and 4, the corresponding fractions are 10^{-4}, 2.8×10^{-4}, 5.2×10^{-4}, and $8.0 \times 10^{-4}\%$.

In the calculations we deliberately did not take into account that in the case of small cycles the values of the equilibrium constants of cyclization do not obey general equations (Appendix, Eqs. XII and XIII) because the effects of small cycles are different for different systems. These effects come from the difference between the real distribution of conformations of short linear oligomers and the distributions governed by Gaussian statistics. Nevertheless, we hope that the relations between the values of the endbiting equilibrium constants and the values of the parameters characterizing the model system investigated will lead to a better understanding of how the reactivity of the endgroups can influence the distribution of macrocycles.

The results of our calculations are collected in Tables 1-5. Inspection of these tables shows that in systems with macromolecules with reactive endgroups, the role of endbiting is manifested by the increasing proportion of monomer units incorporated into the cyclic molecules $(f_{m,c})$, by the increasing number-average degrees of polymerization of the linear macromolecules $(\bar{D}(\ ))$ and of cyclics with and without active centers $(\bar{D}(c)$ and $\bar{D}(m)$, respectively) with an increase of $K_{e(1)}$. These dependencies are more evident for high initiator concentrations. An increase of $\bar{D}(m)$ with increasing $K_{e(1)}$ is, however, limited. It follows from Eqs. (10) and (14) and from the definition $\bar{D}(m) = m'/m_t = \Phi(q,3/2)/\Phi(q,5/2)$ that the maximal value of $\bar{D}(m)$ equals 1.948 and is obtained for q approaching 1 [5].

It is worth noting that even if the number-average degrees of polymerization of linear and cyclic macromolecules $(\bar{D}(l), \bar{D}(m),$ and $\bar{D}(c))$ increase with the stronger endbiting, the number-average degree of polymerization of all macromolecules, cyclic and linear,

TABLE 1. Proportion of Monomer Incorporated into Macrocycles ($f_{m,c}$) for Different Monomer and Initiator Concentrations and for Different Values of $K_{e(1)}$

$K_{e(1)}$	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}
			$[m_1]_0 = 1.5$		
10^{-2}	0.160	0.740	0.955	0.995	1.000
1	0.516	0.796	0.963	0.996	1.000
10^2	0.988	0.984	0.998	1.000	1.000
10^4	1.000	1.000	1.000	1.000	1.000
10^6	1.000	1.000	1.000	1.000	1.000
			$[m_1]_0 = 2.0$		
10^{-2}	0.217	0.690	0.915	0.987	0.999
1	0.497	0.732	0.921	0.988	0.999
10^2	0.983	0.965	0.987	0.998	1.000
10^4	1.000	1.000	1.000	1.000	1.000
10^6	1.000	1.000	1.000	1.000	1.000
			$[m_1]_0 = 3.0$		
10^{-2}	0.245	0.573	0.741	0.818	0.852
1	0.436	0.595	0.743	0.818	0.852
10^2	0.960	0.816	0.794	0.826	0.852
10^4	1.000	0.987	0.900	0.862	0.872
10^6	1.000	1.000	0.987	0.908	0.878

$[m_1]_0 = 4.0$

10^{-2}	0.238	0.475	0.584	0.629	0.653
1	0.377	0.487	0.585	0.629	0.653
10^2	0.914	0.658	0.614	0.631	0.653
10^4	0.999	0.912	0.704	0.654	0.654
10^6	1.000	0.998	0.844	0.693	0.660

$[m_1]_0 = 5.0$

10^{-2}	0.223	0.401	0.478	0.507	0.522
1	0.330	0.409	0.478	0.507	0.522
10^2	0.850	0.545	0.497	0.509	0.522
10^4	0.997	0.810	0.574	0.525	0.524
10^6	1.000	0.991	0.711	0.559	0.529

$[m_1]_0 = 10.0$

10^{-2}	0.154	0.222	0.248	0.257	0.261
1	0.198	0.225	0.248	0.257	0.261
10^2	0.569	0.289	0.254	0.257	0.261
10^4	0.956	0.493	0.298	0.267	0.261
10^6	1.000	0.840	0.395	0.285	0.262

TABLE 2. The Number-Average Degree of Polymerization of Neutral Macrocycles ($\bar{D}(m)$) for Different Initial Monomer and Initiator Concentrations and for Different Values of $K_{e(1)}$

$K_{e(1)}$	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}
		$[m_1]_0 = 1.5$			
10^{-2}	1.043	1.251	1.352	1.373	1.375
1	1.051	1.262	1.355	1.373	1.375
10^2	1.067	1.308	1.367	1.375	1.375
10^4	1.067	1.311	1.368	1.375	1.375
10^6	1.067	1.311	1.368	1.375	1.375
		$[m_1]_0 = 2.0$			
10^{-2}	1.082	1.334	1.504	1.568	1.580
1	1.097	1.348	1.508	1.569	1.580
10^2	1.136	1.443	1.554	1.578	1.581
10^4	1.138	1.459	1.563	1.579	1.581
10^6	1.138	1.459	1.563	1.579	1.581
		$[m_1]_0 = 3.0$			
10^{-2}	1.150	1.458	1.695	1.835	1.906
1	1.173	1.471	1.697	1.835	1.906
10^2	1.270	1.612	1.756	1.847	1.907
10^4	1.279	1.713	1.857	1.900	1.948
10^6	1.280	1.720	1.898	1.948	1.948

$[m_1]_0 = 4.0$

10^{-2}	1.205	1.535	1.762	1.876	1.948
1	1.231	1.544	1.763	1.876	1.948
10^2	1.377	1.672	1.799	1.881	1.948
10^4	1.405	1.801	1.882	1.914	1.948
10^6	1.406	1.824	1.948	1.948	1.948

$[m_1]_0 = 5.0$

10^{-2}	1.250	1.584	1.793	1.892	1.948
1	1.276	1.591	1.794	1.892	1.948
10^2	1.450	1.703	1.819	1.894	1.948
10^4	1.504	1.829	1.891	1.919	1.948
10^6	1.505	1.865	1.948	1.948	1.948

$[m_1]_0 = 10.0$

10^{-2}	1.389	1.695	1.850	1.915	1.948
1	1.409	1.698	1.850	1.915	1.948
10^2	1.594	1.763	1.860	1.916	1.948
10^4	1.720	1.867	1.907	1.947	1.948
10^6	1.729	1.913	1.948	1.948	1.948

TABLE 3. The Number-Average Degree of Polymerization of Macrocycles with Active Center ($\bar{D}(c)$)) for Different Initial Monomer and Initiator Concentrations and for Different Values of $K_{e(1)}$

$K_{e(1)}$	$[i]_0$				
	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}
			$[m_1]_0 = 1.5$		
10^{-2}	1.090	1.681	2.118	2.228	2.242
1	1.107	1.723	2.132	2.230	2.242
10^2	1.144	1.910	2.197	2.238	2.243
10^4	1.145	1.924	2.201	2.239	2.243
10^6	1.145	1.924	2.201	2.239	2.243
			$[m_1]_0 = 2.0$		
10^{-2}	1.180	2.033	3.157	3.867	4.018
1	1.216	2.100	3.196	3.876	4.019
10^2	1.318	2.662	3.683	3.991	4.032
10^4	1.323	2.781	3.798	4.011	4.034
10^6	1.323	2.783	3.799	4.011	4.034
			$[m_1]_0 = 3.0$		
10^{-2}	1.356	2.777	6.454	1.74×10^1	4.90×10^1
1	1.422	2.871	6.520	1.74×10^1	4.90×10^1
10^2	1.754	4.514	9.111	1.98×10^1	5.02×10^1
10^4	1.792	7.091	2.22×10^1	4.35×10^1	7.44×10^1
10^6	1.793	7.334	4.16×10^1	1.12×10^2	2.14×10^2

$[m_1]_0 = 4.0$

1.523	3.467	9.443	2.88×10^1	7.99×10^1
1.610	3.566	9.501	2.88×10^1	8.00×10^1
2.250	5.790	1.24×10^1	3.07×10^1	8.07×10^1
2.415	1.26×10^1	3.15×10^1	5.97×10^1	1.12×10^2
2.417	1.56×10^1	7.68×10^1	1.62×10^2	3.00×10^2

$[m_1]_0 = 5.0$

1.678	4.083	1.19×10^1	3.69×10^1	1.05×10^2
1.778	4.180	1.19×10^1	3.69×10^1	1.05×10^2
2.716	6.705	1.49×10^1	3.85×10^1	1.05×10^2
3.158	1.64×10^1	3.67×10^1	6.91×10^1	1.35×10^2
3.168	2.46×10^1	9.48×10^1	1.88×10^2	3.46×10^2

$[m_1]_0 = 10.0$

2.320	6.455	2.05×10^1	6.27×10^1	1.84×10^2
2.439	6.534	2.05×10^1	6.27×10^1	1.84×10^2
4.227	9.540	2.30×10^1	6.37×10^1	1.84×10^2
7.330	2.54×10^1	4.99×10^1	9.10×10^1	2.04×10^2
7.714	5.85×10^1	1.36×10^2	2.54×10^2	4.68×10^2

Row labels: 10^{-2}, 1, 10^2, 10^4, 10^6

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TABLE 4. The Number-Average Degree of Polymerization of the Total Fraction of Macrocycles $(\bar{D}(m,c))$ for Different Initial Monomer and Initiator Concentrations and for Different Values of $K_{e(1)}$

$K_{e(1)}$	$[i]_0$				
	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}
	$[m_1]_0 = 1.5$				
10^{-2}	1.045	1.251	1.352	1.373	1.375
1	1.087	1.275	1.356	1.373	1.376
10^2	1.125	1.361	1.374	1.375	1.376
10^4	1.126	1.367	1.375	1.376	1.376
10^6	1.126	1.367	1.375	1.376	1.376
	$[m_1]_0 = 2.0$				
10^{-2}	1.084	1.335	1.504	1.568	1.580
1	1.153	1.362	1.509	1.569	1.580
10^2	1.250	1.534	1.569	1.580	1.581
10^4	1.254	1.562	1.581	1.581	1.581
10^6	1.254	1.563	1.581	1.581	1.581
	$[m_1]_0 = 3.0$				
10^{-2}	1.152	1.459	1.695	1.835	1.906
1	1.255	1.485	1.698	1.835	1.906
10^2	1.518	1.793	1.789	1.851	1.907
10^4	1.543	2.092	2.002	1.928	1.952
10^6	1.544	2.116	2.192	2.029	1.963

$[m_1]_0 = 4.0$

10^{-2}	1.207	1.535	1.762	1.876	1.948
1	1.328	1.557	1.763	1.877	1.948
10^2	1.784	1.905	1.835	1.884	1.948
10^4	1.880	2.548	2.088	1.948	1.952
10^6	1.881	2.780	2.499	2.065	1.969

$[m_1]_0 = 5.0$

10^{-2}	1.252	1.584	1.793	1.892	1.948
1	1.383	1.603	1.795	1.892	1.948
10^2	2.013	1.966	1.856	1.897	1.948
10^4	2.250	2.825	2.127	1.956	1.952
10^6	2.250	3.442	2.630	2.083	1.971

$[m_1]_0 = 10.0$

10^{-2}	1.391	1.695	1.850	1.915	1.948
1	1.535	1.708	1.851	1.915	1.948
10^2	2.661	2.089	1.982	1.918	1.948
10^4	4.133	3.434	2.208	1.987	1.951
10^6	4.309	5.827	2.924	2.126	1.977

TABLE 5. The Number-Average Degree of Polymerization of Linear Macromolecules ($\bar{D}(1)$) for Different Initial Monomer and Initiator Concentrations and for Different Values of $K_{e(1)}$

$K_{e(1)}$	$[i]_0$				
	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}
$[m_1]_0 = 1.5$					
10^{-2}	1.271	3.916	6.845	7.715	7.824
1	1.328	4.167	6.954	7.730	7.825
10^2	1.451	5.352	7.464	7.797	7.833
10^4	1.455	5.444	7.496	7.800	7.833
10^6	1.455	5.445	7.496	7.800	7.833
$[m_1]_0 = 2.0$					
10^{-2}	1.577	6.209	1.71×10^1	2.67×10^1	2.89×10^1
1	1.708	6.707	1.76×10^1	2.68×10^1	2.90×10^1
10^2	2.114	1.16×10^1	2.40×10^1	2.85×10^1	2.92×10^1
10^4	2.135	1.29×10^1	2.56×10^1	2.88×10^1	2.92×10^1
10^6	2.136	1.29×10^1	2.57×10^1	2.88×10^1	2.92×10^1
$[m_1]_0 = 3.0$					
10^{-2}	2.278	1.28×10^1	7.78×10^1	5.47×10^2	4.44×10^3
1	2.575	1.38×10^1	7.94×10^1	5.49×10^2	4.44×10^3
10^2	4.347	3.71×10^1	1.55×10^2	7.07×10^2	4.67×10^3
10^4	4.584	9.41×10^1	8.80×10^2	3.46×10^3	1.21×10^4
10^6	4.587	1.01×10^2	3.16×10^3	2.71×10^4	9.98×10^4

$[m_1]_0 = 4.0$

10^{-2}	3.062	2.12×10^1	1.66×10^2	1.49×10^3	1.39×10^4
1	3.518	2.24×10^1	1.68×10^2	1.49×10^3	1.39×10^4
10^2	7.889	6.23×10^1	2.85×10^2	1.70×10^3	1.41×10^4
10^4	9.303	2.93×10^2	1.79×10^3	6.70×10^3	2.71×10^4
10^6	9.325	4.40×10^2	1.28×10^4	5.73×10^4	1.95×10^5

$[m_1]_0 = 5.0$

10^{-2}	3.902	3.00×10^1	2.61×10^2	2.46×10^3	2.39×10^4
1	4.497	3.15×10^1	2.63×10^2	2.47×10^3	2.39×10^4
10^2	1.22×10^1	8.40×10^1	4.03×10^2	2.69×10^3	2.41×10^4
10^4	1.71×10^1	4.87×10^2	2.43×10^3	9.10×10^3	3.96×10^4
10^6	1.72×10^1	1.08×10^3	1.95×10^4	7.70×10^4	2.60×10^5

$[m_1]_0 = 10.0$

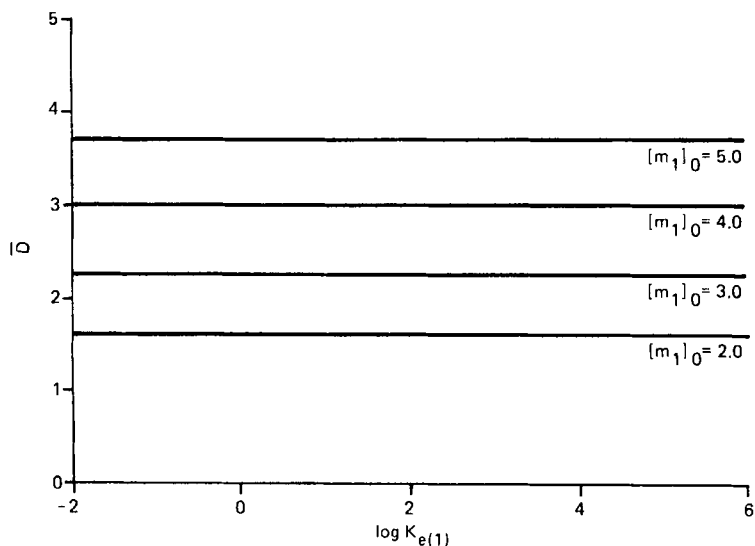|					
10^{-2}	8.475	7.78×10^1	7.52×10^2	7.43×10^3	7.39×10^4
1	9.523	7.97×10^1	7.55×10^2	7.43×10^3	7.39×10^4
10^2	3.23×10^1	1.70×10^2	9.43×10^2	7.67×10^3	7.41×10^4
10^4	1.00×10^2	1.15×10^3	4.60×10^3	1.80×10^4	9.43×10^4
10^6	1.11×10^2	6.42×10^3	4.01×10^4	1.40×10^5	4.76×10^5

FIG. 1. Dependence of the number-average degree of polymeriza-
tion of cyclic and linear macromolecules ($\overline{D}$) on log $K_{e(1)}$. Initial
initiator concentration $[i]_0 = 10^{-2}$.

$$\overline{D} = [m_1]_0/(1_t + m_t + c_t) = \overline{D}(m,c)\overline{D}(l)/[\overline{D}(m,c) + f_{m,c}(\overline{D}(l) - \overline{D}(m,c)]$$

is practically independent of $K_{e(1)}$, as illustrated in Fig. 1. This is
because the increase of the end-to-end cyclization (higher values of
$K_{e(1)}$) results mainly in the conversion of a larger part of the linear
macromolecules into macrocycles with active centers but practically
does not affect the total number of macromolecules in the system.

Experimental Evidence of the Influence of Endbiting on the Equilibrium Distribution of Macrocycles

The relations between the tabulated quantities, depending on the dis-
tribution of macromolecules, and the values of the equilibrium con-
stants of endbiting stem from the influence of the nature of the end-
groups (usually determined by the nature of the initiator used) on the
overall thermodynamics of the polymerization processes. Such an in-
fluence can often be neglected because of low initiator concentrations.
There are, however, examples indicating that in the cationic polymer-
ization of cyclic acetals [8, 9] and of tetrahydrofuran [3], the fractions
of macrocycles observed in processes initiated with protonic acids are

considerably higher than in the case of other initiators, and, as mentioned earlier, this difference may result from efficient endbiting. In each particular case it is necessary, however, to explain whether the increased concentration of macrocycles results from the influence of endbiting on the equilibrium distribution or whether it results from endbiting kinetic enhancement in macrocycles, as described by us previously [4].

In some cases the available experimental data enable discrimination between the two cases mentioned above. For example, Pruckmayr reported on the increased formation of macrocycles in the polymerization of tetrahydrofuran initiated with CF_3SO_3H when compared with a similar polymerization process initiated with $CF_3SO_3CH_3$ [3]. In the polymerization of tetrahydrofuran initiated with CF_3SO_3H, monomer conversion into the linear polymer approaches its maximal value before the highest values of the concentrations of macrocycles are achieved [3], whereas, as we have shown previously [4], in the process with a kinetic enhancement in macrocycles the reverse should be observed. Moreover, in THF polymerization initiated with CF_3SO_3H, the concentrations of macrocycles increase steadily during the entire polymerization. On the other hand, in the process with kinetic enhancement in macrocycles, the concentrations of macrocycles should pass through maxima at an early stage of polymerization. Thus, it is concluded that endbiting influences the equilibrium distribution of cyclics in the polymerization of tetrahydrofuran initiated with CF_3SO_3H.

APPENDIX

Equations Describing the Distribution of Cyclic and Linear Macromolecules in Polymerization with Backbiting and Endbiting Reactions

In polymerization proceeding according to Scheme (2), the equilibrium concentrations of the individual species are related as follows:

$$[L_{n+m}] = K_{p(m)}[M_m][L_n] \tag{I}$$

$$[C_n] = K_{e(n)}[L_n] \tag{II}$$

Equation (I) can be used for derivation of the recurrent formula

$$[L_n] = K_{p(1)}[M_1][L_{n-1}] \tag{III}$$

and thus

$$[L_n] = (K_{p(1)}[M_1])^{n-1}[L_1] \tag{IV}$$

By combining Eqs. (I) and (IV), we obtain

$$[M_m] = [L_{m+n}]/(K_{p(m)}[L_n]) = (K_{p(1)}[M_1])^m/K_{p(m)} \tag{V}$$

Because in Eq. (V), n and m are the current indexes (n = 1, 2, 3, . . .; m = 1, 2, 3, . . .), we can also write

$$[M_n] = (K_{p(1)}[M_1])^n/K_{p(n)} \tag{Va}$$

From Eqs. (II) and (IV) it follows that

$$[C_n] = K_{e(n)}[L_1] (K_{p(1)}[M_1])^{n-1} \tag{VI}$$

The equilibrium constants can be expressed by the corresponding rate constants

$$K_{p(n)} = k_{p(n)}/k_{d(n)} \tag{VII}$$

$$K_{e(n)} = k_{e(n)}/k_o \tag{VIII}$$

where $k_{p(n)}$ and $k_{d(n)}$ are the propagation and backbiting rate constants, respectively, whereas $k_{e(n)}$ and k_o are the rate constants of endbiting and ring-opening. The values of the rate constants of reactions in which macrocycles with n monomer units are formed were assumed to be proportional to the probability of finding both reacting groups closing a properly oriented ring and at a distance necessary to allow a chemical reaction. According to Kuhn [10], for chains obeying Gaussian statistics, this probability is proportional to $n^{-3/2}$. Thus,

$$k_{d(n)} = k_d n^{-3/2} \tag{IX}$$

$$k_{e(n)} = k_e n^{-3/2} \tag{X}$$

where k_d and k_e are the constants characteristic for each type of reaction.

In the dependence of the propagation rate constant $(k_{p(n)})$ on n, the statistical factor has been taken into account, i.e., $k_{p(n)}$ was assumed

to be proportional to the number of groups in the macrocycle which can be attacked by the active centers. Thus,

$$k_{p(n)} = k_p n \tag{XI}$$

For the nonstrained cycles, the rate constants of ring-opening (k_o) were assumed to be independent of the ring size.

From Eqs. (VII)-(XI) it follows that

$$K_p(n) = K_p n^{5/2} \qquad (K_p = k_p/k_d) \tag{XII}$$

$$K_{e(n)} = K_e n^{-3/2} \qquad (K_e = k_e/k_o) \tag{XIII}$$

Denoting in Eqs. (IV)-(VI) that $q = K_{p(1)}[M_1]$, and substituting in Eqs. (Va) and (VI) the expressions for $K_{p(n)}$ and $K_{e(n)}$ (Eqs. XII and XIII), one obtains

$$[L_n] = [L_1]q^{n-1} \tag{XIV}$$

$$[M_n] = q^n/(K_{p(1)}n^{5/2}) \tag{XV}$$

$$[C_n] = K_{e(1)}[L_1] q^{n-1}/n^{3/2} \tag{XVI}$$

$[L_1]$ can be eliminated from Eqs. (XIV) and (XVI) by taking into account that the total concentration of the molecules with active centers is equal to the initial initiator concentration:

$$[I]_0 = \sum_{n=1}^{\infty} [L_n] + \sum_{n=1}^{\infty} [C_n] \tag{XVII}$$

Summations indicated in Eq. (XVII) lead to

$$[I]_0 = [L_1]/(1 - q) + K_{e(1)}[L_1] \Phi(q, 3/2)/q \tag{XVIII}$$

where

$$\Phi(q, 3/2) = \sum_{n=1}^{\infty} q^n/n^{3/2}$$

and

$$[L_1] = [I]_0 q/[K_{e(1)} \Phi(q, 3/2) + q/(1 - q)] \tag{XIX}$$

Thus, substitution of the expressions for $[L_1]$ (Eq. XIX) in Eqs. (XIV) and (XVI) leads to the final equations describing the distribution of cyclic and linear macromolecules:

$$[L_n] = \{[I]_0/[K_{e(1)}\Phi(q,3/2) + q/(1-q)]\}\, q^n \tag{XX}$$

$$[M_n] = (1/K_{p(1)})q^n/n^{5/2} \tag{XXI}$$

$$[C_n] = \{[I]_0 K_{e(1)}/[K_{e(1)}\Phi(q,3/2) + q/(1 - q)]\}\, q^n/n^{3/2} \tag{XXII}$$

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