to 1.55, which was assumed by Domb and Barrett[8] in deriving a semiempirical expression for $\alpha_s^2(z)$. Though not shown here, the α_s^2 vs. z relation given by eq 13 agrees closely with the Domb–Barrett equation[8] over the entire range of positive z, a maximum deviation of about 4% occurring at $z \sim 1$. Thus, eq 13 may be used as a substitute for the Domb–Barrett equation.

Finally, we note that eq 9 gives ν_G which increases monotonically from 1 to 1.2 as N is increased. This can be expected, because $\nu_r(t)$ given by eq 7 is a similar function of t.

References and Notes

(1) Farnoux, B.; Boué, F.; Cotton, J. P.; Daoud, M.; Jannink, G.; Nierlich, M.; de Gennes, P. G. *J. Phys. (Paris)* **1978**, *39*, 77.
(2) Weil, G.; des Cloizeaux, J. *J. Phys. (Paris)* **1979**, *40*, 99.
(3) Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.
(4) François, J.; Schwartz, T.; Weil, G. *Macromolecules* **1980**, *13*, 564.
(5) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(6) Zimm, B. H.; Stockmayer, W. H.; Fixman, M. *J. Chem. Phys.* **1953**, *21*, 1716.
(7) Domb, C.; Barrett, A. J.; Lax, M. *J. Phys. A: Math., Nucl., Gen.* **1973**, *6*, L82.
(8) Domb, C.; Barrett, A. J. *Polymer* **1976**, *17*, 179. Tanaka, G. *Macromolecules* **1980**, *13*, 1513.
(9) Barrett, A. J. *J. Phys. A: Math., Nucl., Gen.* **1976**, *9*, L33.
(10) Lax, M.; Barrett, A. J.; Domb, C. *J. Phys. A: Math., Nucl., Gen.* **1978**, *11*, 361.

Kinetics and Thermodynamics of Cationic Polymerization of 3-Methyltetrahydrofuran

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Received December 8, 1980

Introduction

The polymerization of tetrahydrofuran (THF) has become the most comprehensively understood cationic polymerization system, and its kinetic and thermodynamic aspects have been thoroughly investigated.[1-5] However, very few studies have dealt with the polymerization of substituted tetrahydrofurans and, in fact, it was thought, from thermodynamic considerations, that these monomers could not polymerize.[6] For example, thermodynamic calculations show that substitution of hydrogen atoms by methyl groups in heterocyclic compounds renders the free energy of polymerization less negative and, hence, polymerization still more difficult. Thus, although Chiang and Rhodes[7] and Stratmann et al.[8] have accomplished the polymerization and copolymerization of 3-methyltetrahydrofuran (MTHF), attempts to polymerize 2-methyltetrahydrofuran have not been successful.[7,9] Moreover, studies reported on the cationic polymerization of MTHF were qualitative and led to the conclusion that, in sharp contrast with what occurs with THF, transfer reactions are present, with the result that the molecular weight of poly(3-methyltetrahydrofuran) (PMTHF) is much lower than that of PTHF.[7]

In order to gain additional insight into the cationic polymerization of heterocycles it is desirable to investigate from a quantitative point of view the kinetic and the thermodynamic aspects of the polymerization of MTHF. These studies may contribute to a better understanding of the influence of the structure on the ring-opening polymerization of heterocycles. Therefore, this investigation focuses on the polymerization of MTHF in the terms expressed above.

Table I
Influence of Temperature on Equilibrium Monomer Concentration and Propagation Rate Constant

T, °C	M_e, mol/L	$10^4 k_p$, L/(mol s)
−12.5	5.5	2.8
−8.0	6.7	4.1
−4.0	7.8	5.8
0.0	8.8	8.2

Experimental Section

Materials. The monomer 3-methyltetrahydrofuran (Fluka) was refluxed successively over potassium hydroxide and over sodium for several hours. It was further distilled in vacuo into a sodium mirror. Acetyl chloride was distilled under a nitrogen atmosphere immediately before use. Silver hexafluoroantimonate was washed in vacuo with SO_2, filtered, and stored under a nitrogen atmosphere in darkness.

Initiator. The initiator (acetyl hexafluoroantimonate) was prepared by reaction of silver hexafluoroantimonate and acetyl chloride at −78 °C in monomer solution. The silver chloride obtained in the reaction was eliminated by filtration. All these operations were carried out under high vacuum.

Polymerization. The polymerization was carried out in bulk at several temperatures in the range 0 to −13 °C. Thermostatic baths were used in which the temperature precision was ±0.05 °C. Conventional dilatometric techniques were used for the polymerization kinetics. The polymerization reaction was terminated with an aqueous solution of sodium carbonate, and the polymers were extracted with benzene and precipitated with methanol. The polymers were then freeze-dried from benzene.

Characterization. The monomer and the polymer were analyzed by ^1H NMR spectroscopy at 60 MHz (Perkin-Elmer R-12). The spectra were analogous to those reported elsewhere.[7] The number-average molecular weight of the polymer was determined with a Knauer vapor pressure osmometer.

Results and Discussion

As stated above, all of the reactions reported here were homogeneous in that the initiator was soluble in MTHF at the given reaction conditions. Assuming that the initiator is quantitatively converted to the growing species, the general kinetic expression of propagation for the system has the form

$$\ln \frac{M_0 - M_e}{M - M_e} = k_p I_0 t \qquad (1)$$

All measurements of equilibrium monomer concentration (M_e) were performed by two different techniques: (a) by gravimetry and (b) by assuming additivity of the specific volumes of the polymer and of the monomer. Both methods gave similar results and the values obtained for M_e are shown in the second column of Table I.

Kinetic results obtained for four temperatures are shown in Figure 1. Analysis of the results clearly indicates that, within experimental error, the polymerization reaction is first order with respect to monomer. The good fit of the experimental data to eq 1 shows that the initiation rate is fast enough to prevent the detection of any induction time. It can be observed that even at the lower temperature, initiation is rapid and quantitative. In this respect, MTHF behaves like THF.

The propagation rate constants were determined from the slopes of the straight lines of Figure 1 and the results obtained are shown in the last column of Table I. The Arrhenius plot gives an activation enthalpy ($\Delta H_p^\ddagger$) of 12 kcal mol^{-1} and an activation entropy ($\Delta S_p^\ddagger$) of −29 cal mol^{-1} K^{-1}, the value of $\Delta H_p^\ddagger$ being similar to that obtained for the bulk polymerization of THF.[4,5,10-12] This similarity, however, may be fortuitous because it has been established[4,12] that $\Delta H_p^\ddagger$ is dependent on the solvating power of the system.

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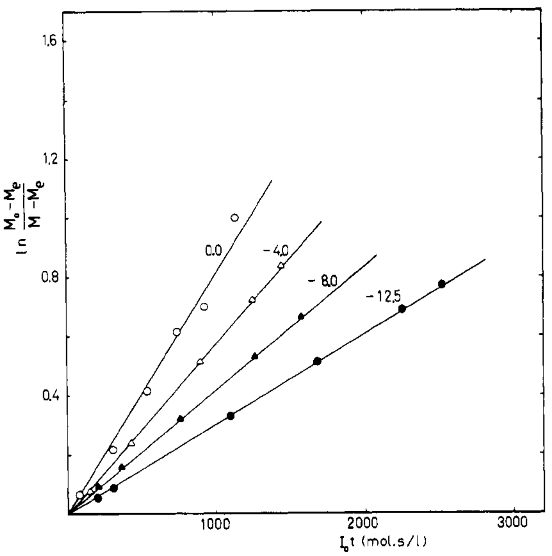

Figure 1. Kinetic results for the polymerization of 3-methyltetrahydrofuran at several temperatures.

Table II
Theoretical $(M_n)_{theor}$ and Experimental $(M_n)_{exptl}$ Number-Average Molecular Weights for Different Polymerization Conditions

T, °C	$10^2 I_0$, mol/L	conversion, %	$(M_n)_{theor}$	$(M_n)_{exptl}$
−4.0	2.56	13	4600	5000
0.0	1.3	9	6600	6600

It has been reported that transfer reactions occur in the bulk polymerization of MTHF which involve hydride ion abstraction from the tertiary carbon;[6] as a result, the growing chains become inactivated and the molecular weight of PMTHF is much lower than that which would be found for PTHF. In other words, the polymerization of MTHF should not have living character. This conclusion is not supported by our results, as can be seen in the second and third columns of Table II, where both the theoretical and experimental values of the number-average molecular weight are shown for two cases. The agreement between both kinds of values rules out the presence of transfer reactions and confirms that the polymerization of MTHF is similar to that of THF. Therefore, initiation, propagation, and depropagation are the only reactions that should occur in the cationic polymerization of MTHF with the catalyst used.

The effect of temperature on monomer equilibrium concentration is shown in Table I. The results clearly show that the values of M_e for MTHF are higher than those for THF (for example, M_e = 1.5–2.6 for THF at 0 °C)[1,4]. This indicates that the free energy of polymerization is less negative for MTHF than it is for THF. Figure 2 shows a plot of depleted monomer at equilibrium as a function of temperature. Extrapolation to $M_0 - M_e = 0$ gives the ceiling temperature, T_c, for the polymerization of MTHF as 4 ± 1 °C. This quantity is significantly lower than that reported for the polymerization of THF, which is in the vicinity of 85 °C.[1]

The equilibrium monomer concentration is related to temperature by the familiar equation

$$\ln M_e = (1/T)(\Delta H_p/R) - \Delta S_p{}^\circ/R \qquad (2)$$

where ΔH_p is the enthalpy of polymerization under the prevailing experimental conditions and $\Delta S_p{}^\circ$ is the entropy change at the standard state (M_e = 1 mol L^{-1}). A plot of ln M_e vs. $1/T$, shown in Figure 3, gives a straight line whose

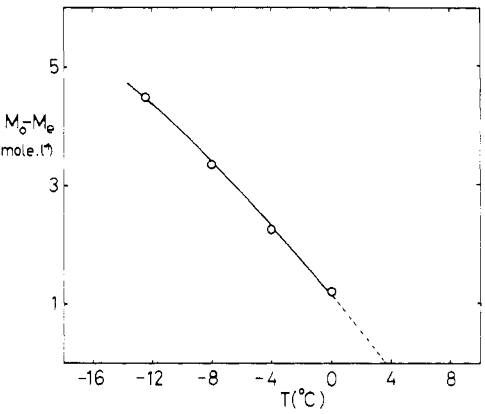

Figure 2. Depleted monomer at equilibrium ($M_0 - M_e$) as a function of temperature.

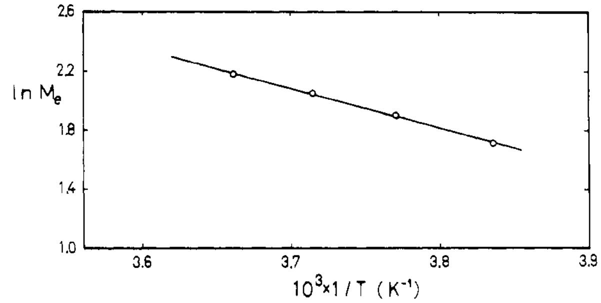

Figure 3. Plot of ln M_e against $1/T$ for the determination of thermodynamic parameters.

slope is $\Delta H_p/R$ and whose intercept gives $-\Delta S_p{}^\circ/R$. From this plot ΔH_p was −5.4 kcal mol^{-1} and $\Delta S_p{}^\circ$ was −24.1 cal K^{-1} mol^{-1}. The value of the former parameter is similar to that obtained for THF.[1] Using the values of ΔH_p and T_c derived above and the equation $T_c = \Delta H_p/\Delta S_p$, we calculated the value of the entropy of bulk polymerization, ΔS_p, to be −19.5 cal K^{-1} mol^{-1}, which is significantly lower than the value found for THF (−12.5 cal K^{-1} mol^{-1}).[1] The cause of this difference is the presence of a methyl group in the repeat unit of PMTHF that reduces the flexibility of the chain.

In conclusion, the results show that the polymerization of MTHF is similar to that of THF. However, the comparatively low value of ΔS_p prevents polymerization of MTHF at temperatures above 4 °C.

Acknowledgment. Thanks are due Dr. J. G. Zilliox of C.R.M. of Strasbourg, France, for supplying the silver hexafluoroantimonate used in this work.

References and Notes

(1) Dreyfuss, P.; Dreyfuss, M. P. *Adv. Polym. Sci.* **1967**, *4*, 528.
(2) Yamashita, Y.; Hirota, M.; Matsui, M.; Hirao, A.; Nobutoki, K. *Polym. J.* **1971**, *1*, 43.
(3) Ledwith, A.; Sherrington, D. C. *Adv. Polym. Sci.* **1975**, *19*, 1.
(4) Matyjaszewski, K.; Slomkowski, S.; Penczek, S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 69.
(5) Croucher, T. G.; Wetton, R. E. *Polymer* **1976**, *17*, 205.
(6) Dainton, F. S.; Ivin, K. J. *Q. Rev., Chem. Soc.* **1958**, *12*, 61.
(7) Chiang, R.; Rhodes, J. H. *Polym. Lett.* **1969**, *7*, 643.
(8) Stratmann, H.; Stützel, B.; Feinauer, R. *Makromol. Chem.* **1978**, *74*, 105.
(9) Kops, J. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1976**, *17*, 182.
(10) Rozenberg, B. A.; Lyudvig, E. B.; Gantmakher, A. R.; Medvedev, S. S. *J. Polym. Sci., Part C* **1967**, *16*, 1917.
(11) Saegusa, T.; Imai, H.; Matsumoto, S. I. *J. Polym. Sci., Part A-1* **1968**, *6*, 459.
(12) Matyjaszewski, K.; Slomkowski, S.; Penczek, S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2413.