equal to zero; we have therefore demonstrated the validity of eq 26.

Acknowledgment. Thanks are due to Professor J. M. Prausnitz for helpful suggestions and comments. The author is also indebted to Italian Consiglio Nazionale delle Ricerche for financial aid during his stay at Berkeley.

References and Notes

(1) J. A. R. Renuncio and J. M. Prausnitz, *Macromolecules*, **9**, 898 (1976).
(2) V. Brandani, *Macromolecules*, **11**, 1293 (1978).
(3) R. L. Scott, *J. Chem. Phys.*, **25**, 193 (1956).
(4) I. Prigogine and A. Bellemans, *Discuss. Faraday Soc.*, **15**, 80 (1953).
(5) I. Prigogine, N. Trappeniers, and V. Mathot, *Discuss. Faraday Soc.*, **15**, 93 (1953).
(6) G. Maurer and J. M. Prausnitz, *Fluid Phase Equilib.*, **2**, 91 (1978).
(7) P. J. Flory, *J. Am. Chem. Soc.*, **89**, 1833 (1965).
(8) G. H. Wilson, *J. Am. Chem. Soc.*, **86**, 127 (1964).
(9) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes", Dover Publications, New York, 1964.
(10) P. J. Flory and H. Höker, *Trans. Faraday Soc.*, **67**, 2258 (1971).
(11) A. W. Francis, *Chem. Eng. Sci.*, **10**, 37 (1959).
(12) A. Bondi, "Physical Properties of Molecular Crystals, Liquids and Glasses", Wiley, New York, 1968.
(13) B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2053 (1968).
(14) B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2061 (1968).
(15) B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2066 (1968).
(16) C. E. H. Bawn and M. A. Wajid, *Trans. Faraday Soc.*, **52**, 1658 (1956).
(17) T. F. Anderson, D. S. Abrams, E. A. Grens, and J. M. Prausnitz, 69th Annual AIChE Meeting, Chicago 1976.
(18) G. L. Nicolaides and C. A. Eckert, *Ind. Eng. Chem., Fundam.*, **17**, 331 (1978).
(19) T. F. Anderson and J. M. Prausnitz, *Ind. Eng. Chem., Prod. Res. Dev.*, **17**, 552 (1978).
(20) C. Watters, H. Daoust, and M. Rinfret, *Can. J. Chem.*, **38**, 1087 (1960).
(21) G. Delmas, D. Patterson, and T. Somcynsky, *J. Polym. Sci.*, **57**, 79 (1962).
(22) G. v. Schulz, K. v. Gunner, and H. Gerrens, *Z. Phys. Chem. (Frankfurt am Main)*, **4**, 192 (1955).
(23) J. A. R. Renuncio and J. M. Prausnitz, *Macromolecules*, **9**, 324 (1976).

Kinetic Study of Polymerization of *trans*-2- and *trans*-3-Oxabicyclo[3.3.0]octane

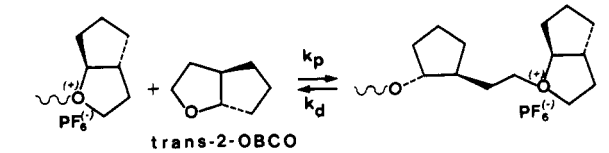
Søren Hvilsted and Jørgen Kops*

Instituttet for Kemiindustri, Technical University of Denmark, DK-2800 Lyngby, Denmark.
Received April 12, 1979

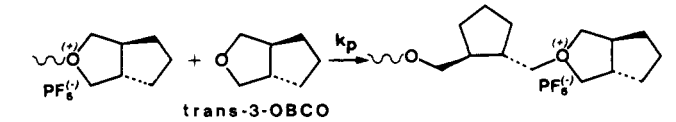
ABSTRACT: The kinetics of polymerization of the two bond-bridged bicyclic ethers, *trans*-2- and *trans*-3-oxabicyclo[3.3.0]octane, have been studied in methylene dichloride initiated by triethyloxonium hexafluorophosphate. The kinetics of both initiation and propagation were investigated by determination of the instantaneous concentration of propagating species at different temperatures in the interval −30 to 0 °C. The initiation reaction is more than three orders of magnitude slower than the propagation reaction. This difference in rate of the reaction of monomer with the triethyloxonium ion and the propagating oxonium ion, respectively, is attributed to the relief of strain in the case of the cyclic ion, and the activation enthalpies are quite different for these reactions ($\Delta H^{\ddagger}_i$ = 74 and 71 kJ·mol^{-1} and $\Delta H^{\ddagger}_p$ = 62 and 56 kJ·mol^{-1} for the two monomers). A mechanism is presented which includes the formation of two types of "dormant" tertiary oxonium ions involving the polymer chains. This mechanism is in accordance with the observed molecular weight distribution and the formation of oligomeric species.

Bond-bridged bicyclic ethers containing an oxacyclopentane ring fused in the trans position have previously been shown to undergo polymerization easily. In the case of compounds with the heterocyclic ring fused with a cyclohexane ring, the polymerization is either partially or completely reversible.[1,2] The fusion of two five-membered rings in trans positions yields a highly strained monomer, thus *trans*-3-oxabicyclo[3.3.0]octane (*trans*-3-OBCO) is very reactive and shows no sign of reversibility,[3] while the corresponding less-strained *cis*-3-oxabicyclo[3.3.0]octane (*cis*-3-OBCO) is completely inactive when contacted with phosphorus pentafluoride initiator.

In this paper, results are reported from a kinetic study of the polymerizations of the two bond-bridged bicyclic ethers, *trans*-2- and *trans*-3-OBCO. The polymerizations have been studied in CH_2Cl_2 in the temperature range −30 to 0 °C, using the salt triethyloxonium hexafluorophosphate (Et_3OPF_6) as the initiator. The mechanisms of chain propagation for the two monomers have also been investigated and already reported in preliminary form.[4] It was shown by ^{13}C NMR that the repeat units of the polymers correspond to ring opening exclusively by nucleophilic attack of monomer oxygen at the methylene carbon adjacent to the oxonium ion at the growing chain end:



trans-2-OBCO



trans-3-OBCO

The initiation and propagation steps are formulated as follows:

$$I + M \xrightarrow{k_i} M^* \quad (1)$$

$$M^* + M \xrightarrow{k_p} P^* \quad (2)$$

$$P^* + M \xrightarrow{k_p} P^* \quad (3)$$

0024-9297/79/2212-0889$01.00/0

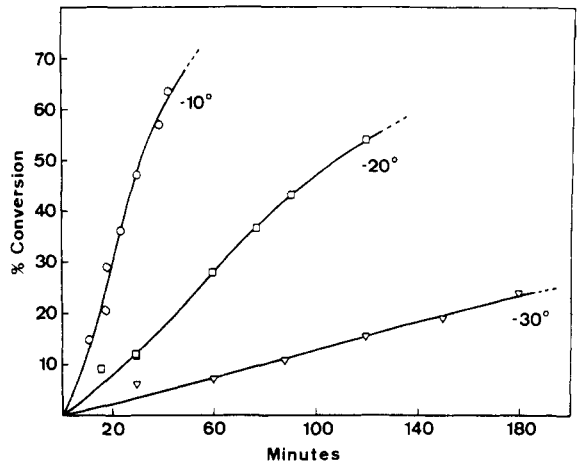


Figure 1. Time–conversion curve in the polymerization of *trans*-3-OBCO.

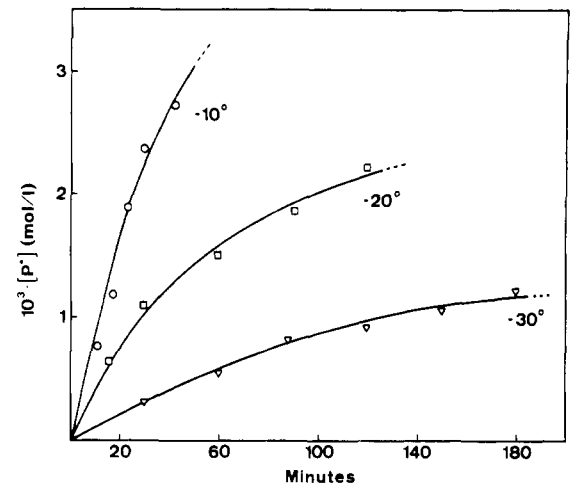


Figure 2. Time–[P*] curve for the polymerization of *trans*-3-OBCO.

and the rate equations integrated with respect to time may be written:

$$\ln \frac{[I]_{t_1}}{[I]_{t_2}} = k_i \int_{t_1}^{t_2} [M]\, dt \quad (4)$$

$$\ln \frac{[M]_{t_1}}{[M]_{t_2}} = k_p \int_{t_1}^{t_2} [P^*]\, dt \quad (5)$$

where [I], [M], and [P*] are the concentrations of initiator, monomer, and active species, and k_i and k_p are the rate constants for initiation and propagation. It is considered that the initially formed active species M* behaves in the same manner as any of the polymeric active species P*. The computation of the rate constants is based on a knowledge of the concentration of active species as determined by Saegusa and Matsumoto's phenoxyl end-capping method.[5] A graphical integration of the change in concentration of active species over a given time interval (eq 5) forms the basis for the calculation of the propagation rate constants. The initiation rate constants are calculated in a similar manner where the change in monomer concentration (eq 4) is obtained from the conversion curve, and the initiator concentrations are determined as explained below.

In the case of *trans*-3-OBCO, complete conversion of monomer is found at 0 °C in accordance with our previous investigation,[3] and for the lower temperature interval (to −30 °C) the propagation is considered as an irreversible process, i.e., the backward reactions (in eq 2 and 3) are omitted and the kinetic treatment is as indicated above. For *trans*-2-OBCO, a certain amount of monomer remained in equilibrium with polymer at the temperatures in the investigated range, −20 to 0 °C. In this case, the rate constant for propagation is calculated on the basis of the integrated rate expression in which the equilibrium monomer concentration $[M]_e$ is included:

$$\ln \frac{[M]_{t_1} - [M]_e}{[M]_{t_2} - [M]_e} = k_p \int_{t_1}^{t_2} [P^*]\, dt \quad (6)$$

The time–conversion curves for *trans*-3-OBCO at three temperatures with $[M]_0$ = 1.49 mol L^{-1} and $[I]_0$ = 0.0081 mol L^{-1} are shown in Figure 1, and the changes in the concentration of active species with time at these temperatures are shown in Figure 2. The plots in Figure 3 of the quantities in the integrated rate eq 5 give linear relationships at all three temperatures, which allow calculation of the values of the propagation rate constants given in Table I. From the Arrhenius plot in Figure 4 is

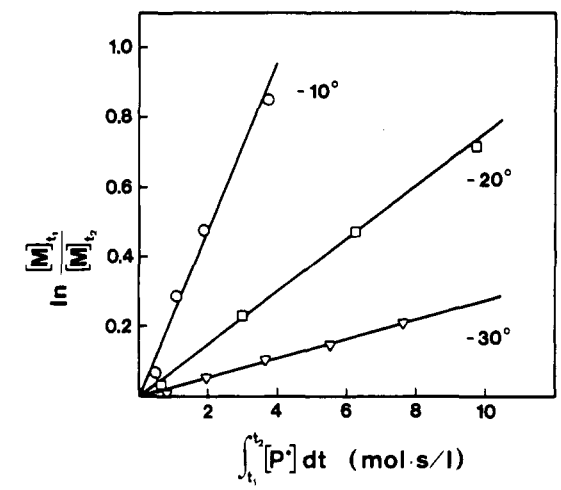


Figure 3. Relationship between $\ln ([M]_{t_1}/[M]_{t_2})$ and $\int_{t_1}^{t_2}[P^*]\,dt$ for polymerization of *trans*-3-OBCO: −10 °C, t_1 = 11 min; −20 °C, t_1 = 15.75 min; −30 °C, t_1 = 30 min.

Table I
Rate Constants and Activation Parameters of the Polymerization of *trans*-2- and *trans*-3-OBCO in CH_2Cl_2 Initiated by Et_3OPF_6

	k_i 10^3 L·mol^{-1}·s^{-1}		k_p, L·mol^{-1}·s^{-1}	
T, °C	*trans*-2-OBCO	*trans*-3-OBCO	*trans*-2-OBCO	*trans*-4-OBCO
0	0.27		0.53	
−10	0.068	0.22	0.14	0.24
−20	0.019	0.047	0.056	0.075
−30		0.014		0.027

	x = initiation		x = propagation	
$\Delta E^{\ddagger}_x$, kJ·mol^{-1}	76	73	64	58
A_x, L·mol^{-1}·s^{-1}	10^{11}	7×10^{10}	10^{12}	8×10^{10}
$\Delta G^{\ddagger}_x$, kJ·mol^{-1} (−20 °C)	85	82	68	67
$\Delta H^{\ddagger}_x$, kJ·mol^{-1}	74	71	62	56
$\Delta S^{\ddagger}_x$, J·mol^{-1}·K^{-1}	−42	−45	−22	−44

calculated the activation energy $\Delta E^{\ddagger}_p$ and frequency factor A_p, which also are given in Table I.

In each experiment, the total concentration of phenyl ether in the sample after the reaction with phenoxide was determined by UV at 272 nm. This concentration, which represents both the phenyl ether groups at the polymer ends as well as the phenyl ethyl ether (phenetole) originating from the reaction with the remaining initiator, was always only slightly less than the nominal concentration

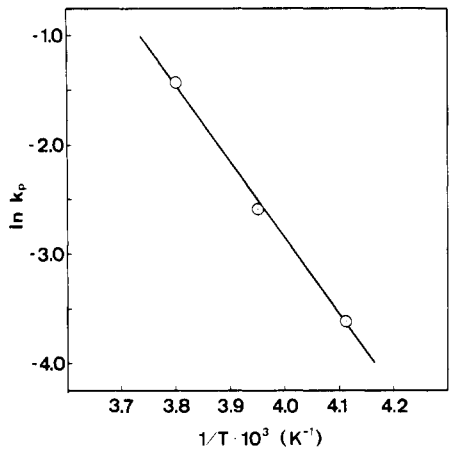


Figure 4. Arrhenius plot of propagation rate constants of the polymerization of *trans*-3-OBCO.

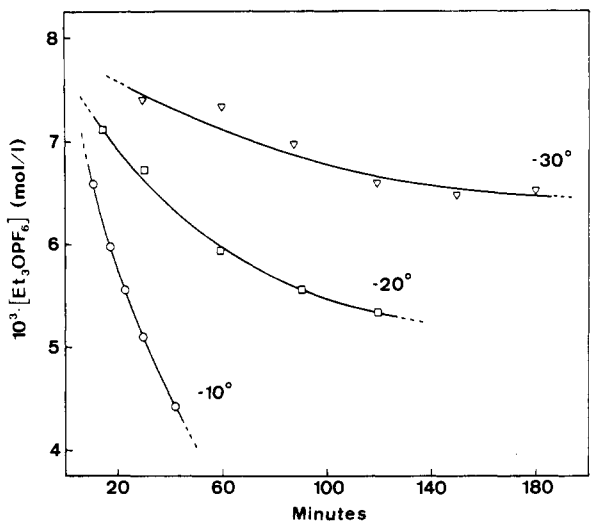


Figure 5. Time–[Et_3OPF_6] curve for the polymerization of *trans*-3-OBCO.

of the added initiator. After the phenetole was removed by vacuum distillation with the aid of decalin as the entrainer[6] and [P*] was determined, the amount of remaining Et_3OPF_6 was found by difference calculation. In Figure 5 is shown the time–[Et_3OPF_6] curves at the three reaction temperatures in the case of polymerization of *trans*-3-OBCO, and in Figure 6 a plot is presented in accordance with the integrated rate expression for initiation (eq 4). The values of the rate constants are given in Table I, and on the basis of the Arrhenius plot in Figure 7, the activation energy and frequency factor were calculated.

The additional kinetic parameters for both initiation and propagation which are listed in Table I were obtained in accordance with transition-state theory and calculated from the relations[7]

$$k_x = \frac{kT}{h} \exp\{-\Delta G^{\ddagger}_x/RT\} \quad (7)$$

$$\Delta H^{\ddagger}_x = \Delta E^{\ddagger}_x - RT \quad (8)$$

$$\Delta G^{\ddagger}_x = \Delta H^{\ddagger}_x - T\Delta S^{\ddagger}_x \quad (9)$$

where k and h are Boltzman's and Planck's constants, respectively, and x refers to either initiation or propagation.

A corresponding kinetic investigation has been carried out for the polymerization of *trans*-2-OBCO under identical conditions; the appropriate plots are shown in Figures 8–14, and the rate constants and activation parameters are summarized in Table I.

The molecular weight values determined by GPC are given in Figures 15 and 16. The GPC curves were in all cases multimodal, indicating the presence of small amounts of oligomers (trimer and tetramer).

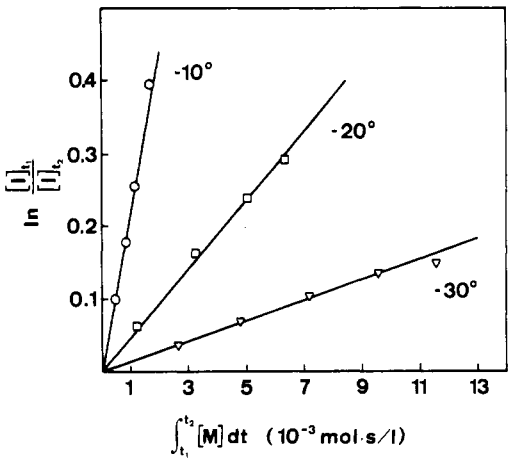


Figure 6. Relationship between ln $([I]_{t_1}/[I]_{t_2})$ and $\int_{t_1}^{t_2}[M]\,dt$ for polymerization of *trans*-3-OBCO: −10 °C, t_1 = 11 min; −20 °C, t_1 = 15.75 min; −30 °C, t_1 = 30 min.

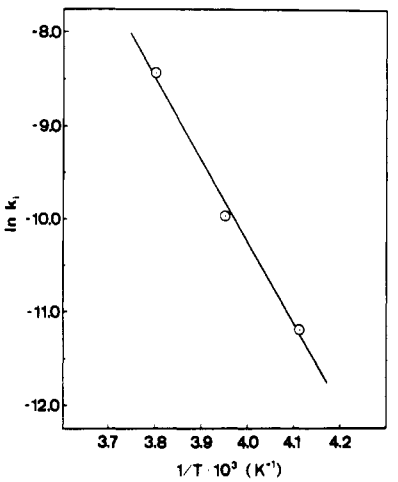


Figure 7. Arrhenius plot of initiation rate constants of the polymerization of *trans*-3-OBCO.

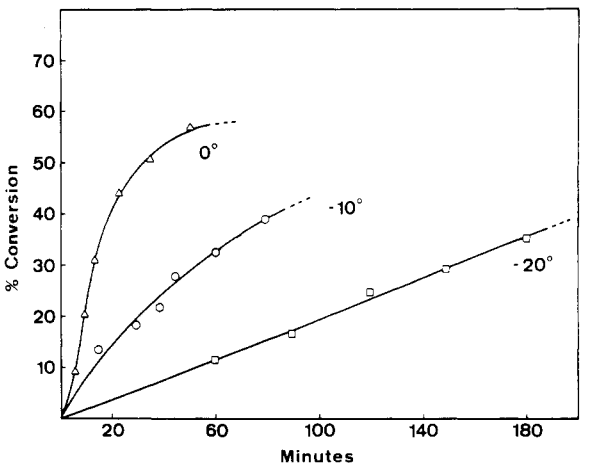


Figure 8. Time–conversion curve in the polymerization of *trans*-2-OBCO.

Discussion

With reference to Table I, it is seen that the initation reaction for both monomers is more than three orders of

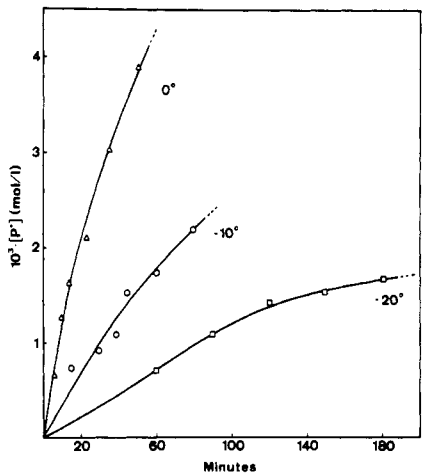


Figure 9. Time–[P*] curve for the polymerization of *trans*-2-OBCO.

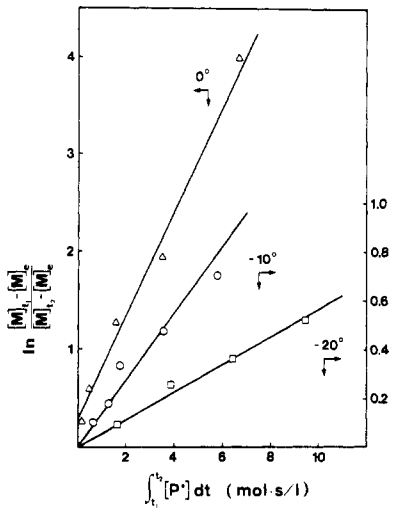


Figure 10. Relationship between ln $((([M]_{t_1} - [M]_e)/([M]_{t_2} - [M]_e))$ and $\int_{t_1}^{t_2}[P^*]\,dt$ for polymerization of *trans*-2-OBCO: 0 °C, $[M]_e$ = 0.63 mol/L, t_1 = 6 min; −10 °C, $[M]_e$ = 0.54 mol/L, t_1 = 15 min; −20 °C, $[M]_e$ = 0.45 mol/L, t_1 = 60 min.

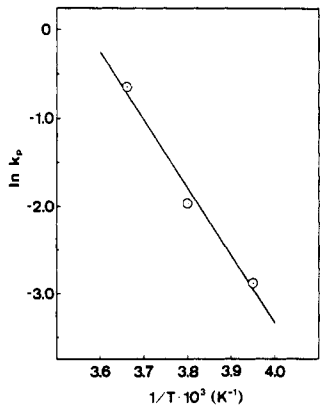


Figure 11. Arrhenius plot of propagation rate constants of the polymerization of *trans*-2-OBCO.

magnitude slower than the propagation reaction. It should be noted that the values in each case represent overall rate constants, which encompass the various contributions to the rate from different species such as free ions and ion pairs. Resolution of these contributions has not been an objective of the present study. A consequence of the slow rate of initiation is the gradual increase in the concentration of active species (Figures 2 and 9), which is noted during the course of the polymerization. Obviously, the

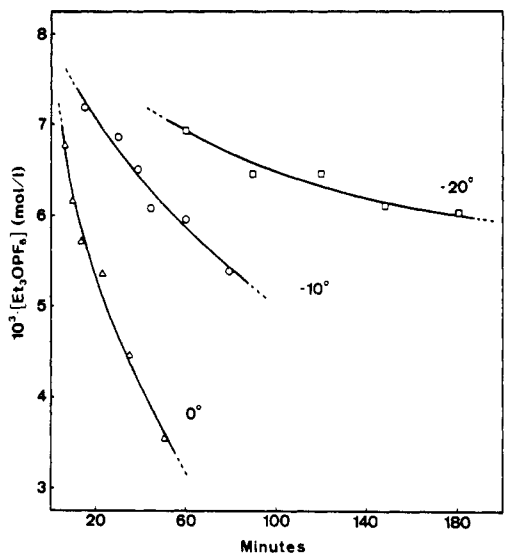


Figure 12. Time–$[Et_3OPF_6]$ curve for the polymerization of *trans*-2-OBCO in CH_2Cl_2.

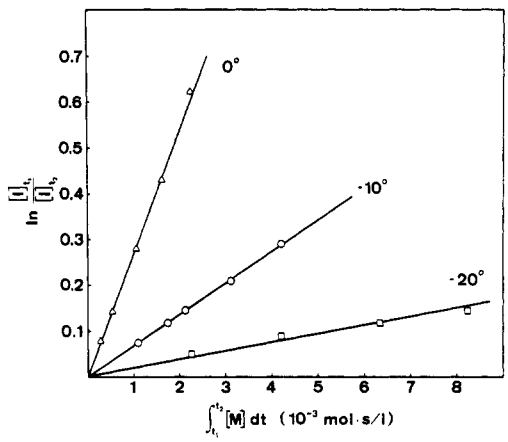


Figure 13. Relationship between ln $([I]_{t_1}/[I]_{t_2})$ and $\int_{t_1}^{t_2}[M]\,dt$ for polymerization of *trans*-2-OBCO: 0 °C, t_1 = 6 min; −10 °C, t_1 = 15 min; −20 °C, t_1 = 60 min.

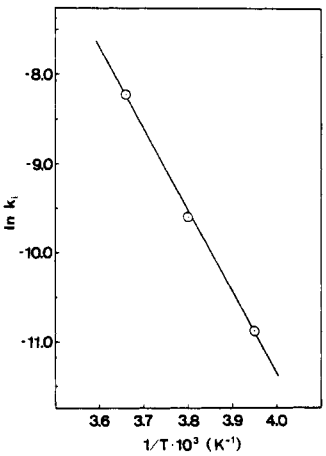


Figure 14. Arrhenius plot of initiation rate constants of the polymerization of *trans*-2-OBCO.

procedure adapted here for the kinetic analysis with the determination of the number of active species present at any given time is indispensable.

Initiation and propagation occur by S_N2 reactions where monomer as nucleophile attacks the triethyloxonium ion (1) or the strained cyclic oxonium ion (2), respectively, as shown in Figure 17 in the case of *trans*-3-OBCO. A similar

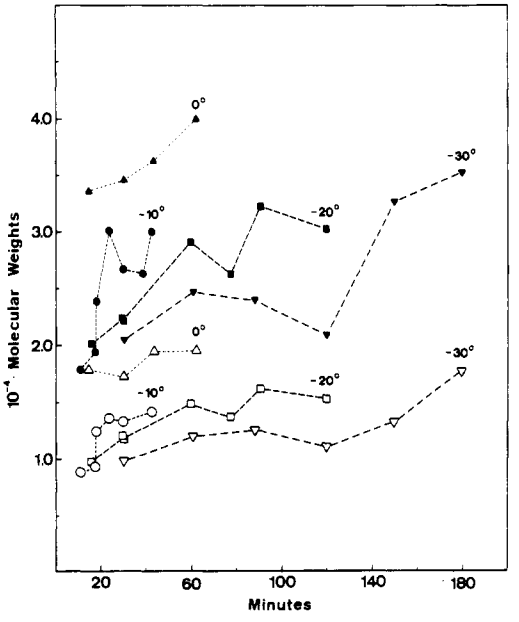


Figure 15. Molecular weights in the polymerization of *trans*-3-OBCO. Open symbols represent $\bar{M}_n$, and filled points represent $\bar{M}_w$.

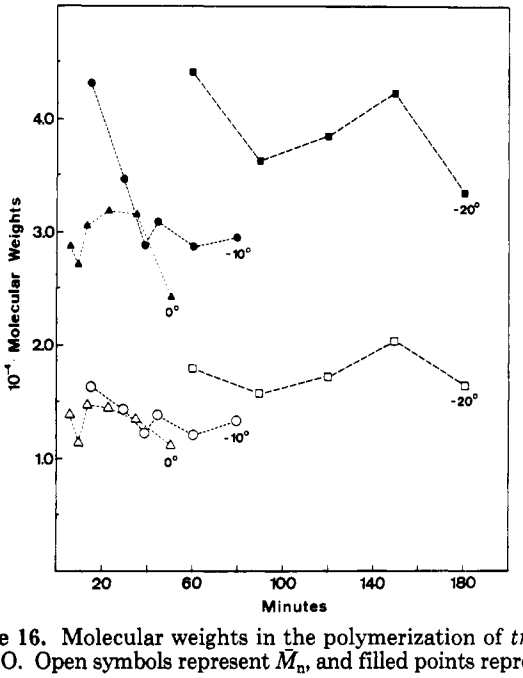


Figure 16. Molecular weights in the polymerization of *trans*-2-OBCO. Open symbols represent $\bar{M}_n$, and filled points represent $\bar{M}_w$.

mechanism applies to the *trans*-2-OBCO polymerization, and a separate scheme is not presented for this monomer. The very large difference in rate between initiation and propagation is seen from Table I to be related particularly to the lower values of the activation enthalpy for the propagation. The lower $\Delta H^{\ddagger}_p$ value is best understood by consideration of the stability of the two oxonium ions. In the case of the triethyloxonium ion with free mobility of the substituents, the structure is essentially strainless, whereas in the case of the propagating oxonium ion a severe strain is found in the cyclic part of the ion which is impossible to relieve, owing to the trans configuration present at the bond bridge. The high strain results in lower stability of the ion, which is reflected in increased reactivity. The propagation of *trans*-2-OBCO takes place a little slower than that of *trans*-3-OBCO. The activation parameters differ to some extent, and a higher activation

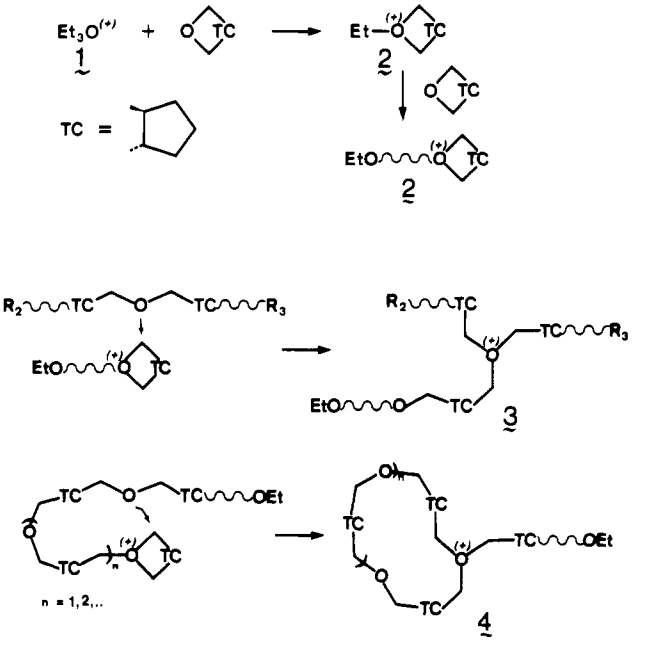


Figure 17. Schematic outline of the mechanism of polymerization of *trans*-3-OBCO initiated with Et_3OPF_6 (the counterion is omitted in the scheme).

enthalpy in the case of *trans*-2-OBCO is partly compensated for by a lower value for the activation entropy ($-\Delta S^{\ddagger}\rho$). Heats of combustion data[8] have indicated that *trans*-3-OBCO is somewhat more strained than *trans*-2-OBCO.

Regarding the actual values for the rate constants and the activation parameters, no direct comparison can be made with literature values since the present investigation is to our knowledge the first detailed kinetic study of the initiation of the polymerization of a cyclic ether with Et_3OPF_6. Previously, the reaction between various monocyclic ethers and Et_3OBF_4 in CH_2Cl_2 was studied in a higher temperature range (2.5–35 °C) by the NMR technique.[9] The study carried out with tetrahydrofuran, tetrahydropyran, and oxepane showed that the rates of alkylation corresponding to initiation in the former and latter case vary little in this series and are in fact slower than the rates reported in the present study. The activation enthalpies of initiation were in the range 68–71 kJ·mol^{-1}, i.e., comparable to the values for the initiation reactions given in Table I. The activation entropies of initiation ($-\Delta S^{\ddagger}_i$) for the same series of monocyclic ethers were in the range 67–71 J·mol^{-1}·K^{-1}. These values are considerably higher than those for the Et_3OPF_6–*trans*-2- and -*trans*-3-OBCO systems. This difference may reflect a difference in the process of desolvation of the ground state due to the charge dispersion in the transition state when the monomer reacts with the initiator. The bicyclic monomer is a larger molecule requiring more space when solvating the oxonium ion, thus allowing fewer solvent molecules in the solvation shell around the oxonium ion. Thus the smaller change in orderedness when fewer molecules are arranged in the solvation shell may explain the more favorable entropies of activation for the initiation process in the case of the bicyclic monomers. A preferential solvation of the oxonium ion by monomer has been assumed also in the case of polymerization of tetrahydrofuran.[10]

The rate constants for propagation are large compared to the constants reported for tetrahydrofuran at 0 °C in CH_2Cl_2 with the same initiator. An overall constant for THF was determined as[11] 4.19×10^{-3} L·mol^{-1}·s^{-1}, while the

constants for propagation via ion pairs and free ions were found to be[12] 0.87 × 10^{-3} and 21 × 10^{-3} L·mol^{-1}·s^{-1}, respectively. The type of counterion in the triethyloxonium salt was found in the latter study to play a minor role for the value of the rate constant. The propagation rates for *trans*-2- and *trans*-3-OBCO are roughly two orders of magnitude higher than the values for THF, and this is also found to be the case for the less strained bicyclic ether *trans*-8-oxabicyclo[4.3.0]nonane.[13] In comparison with atom-bridged bicyclic substituted monomers of the 7-oxabicyclo[2.2.1]heptane series,[14,15] the rates are also much higher, although a different initiator system was used for these monomers.

The polymerizations appear from the determination of the number of active species to proceed without actual termination. However, transfer reactions occur extensively. It is suggested in the mechanistic scheme for the polymerization in Figure 17 that the cyclic oxonium ions may be attacked not only by monomer oxygen but also by oxygen in the polymer chains either inter- or intramolecularly. The resulting acyclic oxonium ion (3) and macrocyclic less strained oxonium ion (4) are considered "dormant" in the sense that the reactivity is as low as that of the triethyloxonium ion. When monomer reacts with the dormant acyclic species by attack at one of the three α positions to the oxonium ion, a regeneration of the active cyclic oxonium ion takes place. By this process, a redistribution of the lengths of growing chains will be effected. A randomization is indicated by the polydispersity index which in all cases is very close to the value of 2 as is apparent from the number and weight average molecular weight values in Figures 15 and 16. This part of the proposed reaction scheme is rather similar to the one suggested for the polymerization of oxetane with hexafluorophosphate salts by Worsfold.[16]

When monomer attacks the exocyclic α-methylene group of the macrocyclic oxonium ion (4), a cyclic oligomer is formed simultaneously with the regeneration of the active small ring oxonium ion. The formation in all the polymerizations of small amounts of oligomers (around 1%) is in accordance with the proposed mechanism. A low concentration of the large ring oxonium ions probably limits the amount of oligomer which is formed. The presence of trimer and tetramers was demonstrated, and with a cyclic structure these will be 15-crown-3 and 20-crown-4 ethers. Whereas the formation of cyclic oligomers in the polymerization of oxetane has long been known and also recently extensively studied by Dreyfuss and Dreyfuss,[17] the formation of such oligomers in the case of polymerization by ring opening of five-membered cyclic ether compounds was only demonstrated recently. In 1976, strong evidence for the formation of cyclic oligomers up to pentamer was reported in the polymerization of the bicyclic ether *trans*-7-oxabicyclo[4.3.0]nonane.[2] Later it was found that even in the case of polymerization of tetrahydrofuran initiated by Me_3OBF_4, triflic acid, and esters, cyclic oligomers are formed.[18,19]

The presence of the dormant species, acyclic as well as macrocyclic, will affect the values for the calculated rate constants since these species are included in determined values for [P*]. As indicated above, the amount of cyclic oligomer which is formed is, however, actually quite small, thus we assume that the correction of the [P*] values and the rate constants and activation parameters will not be large in our case. However, it should be kept in mind that for these monomers, and probably in the case of other polymerization systems involving the opening of an oxacyclopentane ring, many different active species may be present, including the ions and ion pairs as already mentioned.

Experimental Section

Materials. The preparations of *trans*-2- and *trans*-3-oxabicyclo[3.3.0]octane are described in detail elsewhere.[20] Briefly, in the case of *trans*-2-OBCO, ethyl 2-oxocyclopentanecarboxylate was reacted with 2-iodoethyl acetate to form ethyl 1-(2-acetoxyethyl)-2-oxocyclopentanecarboxylate. This compound was converted with HBr to the bromo ketone, 2-(2-bromoethyl)-cyclopentanone, which after reduction with $NaBH_4$ to *trans*-2-(2-bromoethyl)cyclopentanol was ring closed to the bicyclic ether by treatment with KOH solution. The *trans*-3-OBCO was prepared starting from pimelic acid which was converted into the diacid chloride followed by bromination and esterification to diethyl 2,6-dibromopimalate. This compound was converted into *trans*-1,2-cyclopentanedicarboxylic acid by first reacting it with sodium cyanide to form the diethyl 1-cyano-1,2-cyclopentanedicarboxylate followed by hydrolysis and decarboxylation. The further procedure for converting the trans diacid followed one published by Owen and Peto[21] and consisted of a reduction to the trans diol followed by mesylation and ring closure by treatment with KOH. The monomers were purified by redistillation on a spinning band column to a purity better than 99.95%. The polymerization solvent CH_2Cl_2 (Merck, p.a.) was purified by consecutive treatments with concentrated H_2SO_4, H_2O, 10% Na_2CO_3, and H_2O and predrying over $CaCl_2$. This was followed by reflux and distillation from P_2O_5 where only a middle fraction was collected. The initiator triethyloxonium hexafluorophosphate was purified by dissolving a 1-g portion in the drybox in 10 mL of pure and dry CH_2Cl_2 and precipitating by adding Et_2O (refluxed and distilled from $LiAlH_4$) and repeating twice. After the precipitate was dried under vacuum and stored under ultrapure nitrogen, the salt had a melting point of 142.0–142.5 °C (lit.[22] mp 142–143 °C). The terminating agent, sodium phenoxide, was prepared in THF (Merck, Uvasol, distilled under nitrogen from $LiAlH_4$) by reacting pure phenol (distilled under N_2) with freshly cut sodium in the drybox. The vessel containing the solution was then fused to a high-vacuum assembly, where the solution was filtered through a sintered glass filter into storage ampules and later redistributed into phials under vacuum conditions.

Polymerization Procedures. The general conditions for all of the solution polymerizations in CH_2Cl_2 initiated with Et_3OPF_6 were $[M]_0$ = 1.49 mol·L^{-1} and $[I]_0$ = 0.0081 mol·L^{-1}. All polymerization experiments were carried out in an all-glass apparatus which was connected to a high-vacuum line where all the necessary operations were performed regarding the preparation of the polymerization charge. The procedures which were used have been very thoroughly described.[20] In brief, the pure, predried monomers were after degassing dried on the vacuum line first with BaO and then a K–Na alloy and finally distilled into storage burets equipped with Rotaflo valves from which the dosing to the polymerization ampules could be performed. The purified and predried CH_2Cl_2 was dried on the vacuum line over freshly sublimed P_2O_5 and then distilled onto a fresh Na mirror before storage in a buret as above. (Note: It has been reported that it is very dangerous to bring CH_2Cl_2 into contact with a Na film except under vacuum and after drying it very carefully![23]) The initiator, a freshly made solution in CH_2Cl_2, was added with a syringe to the polymerization ampule, the solvent was removed, and thorough drying of the salt was performed by evacuation prior to charging the monomer and the solvent. The necessary amount of sodium phenoxide for the end capping was enclosed in a phial in the polymerization ampule, and it was introduced at the appropriate time by breaking the phial. The terminated polymer solution was washed and dried and divided into one part which was used for yield determination after evaporation to dryness and another part which was used for the determinations of the phenyl ether content by UV analysis.

Apparatus. The molecular weights were obtained by gel-permeation chromatography in THF solution, using Waters Model 200 instrument. Two sets of columns were used, either 10^6, 2 × 10^4, 10^4, and 10^3 Å or 2000, 500, 100, and 60 Å. The molecular weight average values were determined on the basis of the extended chain length method and a Q value of 18.4 g·mol^{-1}·Å^{-1}. These molecular weight values were adequate for studying the

effects of the changes in the polymerization conditions. The UV analyses were performed in CH_2Cl_2 at room temperature at 225 to 325 nm, using a Beekman DK-2A ratio recording spectrophotometer.

Acknowledgment. The financial support of this research project by the National Research Council of Denmark (Statens tekniskvidenskabelige Forskningsråd) is gratefully acknowledged. Many thanks are due to Professor Peter H. Plesch for the help with developing the experimental technique during a 2-week stay in 1976 at the University of Keele by one of us (S.H.). A gift of the triethyloxonium hexafluorophosphate by Dr. Patricia Dreyfuss, University of Akron, is appreciated, and finally many thanks are due to Mr. Hans Spanggaard of this Institute for interesting and helpful discussions and suggestions with regard to the performed work.

References and Notes

(1) J. Kops and H. Spanggaard, *Makromol. Chem.*, **175**, 3077 (1974).
(2) J. Kops, E. Larsen, and H. Spanggaard, *J. Polym. Sci., Polym. Symp.*, **56**, 91 (1976).
(3) J. Kops, S. Hvilsted, and G. Sørensen, *Proc. Int. Symp. Polymeriz. Heterocycles (Ring-Opening), 1st*, 132 (1975).
(4) J. Kops, S. Hvilsted, and H. Spanggaard, *Proc. Eur. Conf. NMR Macromol.*, 109 (1978).
(5) T. Saegusa and S. Matsumoto, *Macromolecules*, **1**, 442 (1968).
(6) T. Saegusa and S. Matsumoto, *J. Macromol. Sci., Chem.*, **4**, 873 (1970).
(7) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", Wiley, New York, 1961, Chapter 5.
(8) M. Procházka, J. V. Cerný, and M. Smisek, *Collect. Czech. Chem. Commun.*, **31**, 1315 (1966).
(9) T. Saegusa, Y. Kimura, H. Fujii, and S. Kobayashi, *Macromolecules*, **6**, 657 (1973).
(10) A. M. Buyle, K. Matyjaszewski, and St. Penczek, *Macromolecules*, **10**, 269 (1977).
(11) Y. Yamashita, S. Kozawa, M. Hirota, K. Chiba, H. Matsui, A. Hirao, M. Kodama, and K. Ito, *Makromol. Chem.*, **142**, 171 (1971).
(12) P. Bourdauducq and D. J. Worsfold, *Macromolecules*, **8**, 562 (1975).
(13) J. Kops and H. Spanggaard, unpublished results.
(14) T. Saegusa, M. Motoi, S. Matsumoto, and H. Fujii, *Macromolecules*, **5**, 815 (1972).
(15) T. Saegusa, M. Motoi, and H. Suda, *Macromolecules*, **9**, 526 (1976).
(16) P. E. Black and D. J. Worsfold, *Can. J. Chem.*, **54**, 3325 (1976).
(17) P. Dreyfuss and M. P. Dreyfuss, *Polym. J.*, **8**, 81 (1976).
(18) J. M. McKenna, T. K. Wu, and G. Pruckmayr, *Macromolecules*, **10**, 877 (1977).
(19) G. Pruckmayr and T. K. Wu, *Macromolecules*, **11**, 265 (1978).
(20) S. Hvilsted, "A Study of Kinetics and Mechanism of Polymerization of *trans*-3- and *trans*-2-Oxabicyclo[3.3.0]octane", Ph.D. Dissertation, submitted to the Faculty of Chemical Engineering, Technical University of Denmark, 1978.
(21) L. N. Owen and A. G. Peto, *J. Chem. Soc.*, 2383 (1955).
(22) P. Dreyfuss and M. P. Dreyfuss, *Adv. Chem. Ser.*, **No. 91**, 335 (1969).
(23) Y. Firat, F. R. Jones, P. H. Plesch, and P. H. Westermann, *Makromol. Chem., Suppl.*, **1**, 203 (1975).

Kinetics and Mechanism of the Bulk Thermal Polymerization of (3-Phenoxyphenyl)acetylene

J. M. Pickard* and E. G. Jones

Research Applications Division, Systems Research Laboratories, Inc., Dayton, Ohio 45440

I. J. Goldfarb

Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio 45433. *Received April 2, 1979*

ABSTRACT: The kinetics of the high-temperature bulk polymerization of (3-phenoxyphenyl)acetylene were examined over the temperature range 400 to 600 K, using differential scanning calorimetry. Analyses of samples polymerized over a wide range of temperature, using gel permeation chromatography, revealed that the polymer molecular weight is invariant with temperature. The absence of an observable temperature correlation for polymer molecular weight is examined in terms of a biradical mechanism in which the kinetic and molecular chain lengths are controlled by a first-order termination step involving cyclization of the growing polymer chain. Based upon the observed data and semiempirical thermochemical arguments, it is concluded that the molecular weight of poly(3-phenoxyphenyl)acetylene is controlled predominantly by steric and thermochemical factors rather than by the reaction energetics.

The mechanisms for thermal polymerization of arylacetylenes are of interest from both theoretical and technological viewpoints. These compounds, in particular phenylacetylene and its simple derivatives, polymerize spontaneously in the range 400 to 600 K, and initiation may involve biradical formation.[1,2] Also, the molecular weight of the resultant polymer is rather insensitive to polymerization temperature.[3,4] The lack of an appreciable temperature dependence for molecular weight has been interpreted in the past as arising from degradative chain transfer[5,6] and more recently as being the result of a size-dependent first-order deactivation of the polymer chains.[4,7]

The 3-phenoxyphenyl substituent in the related monomer, (3-phenoxyphenyl)acetylene, occurs frequently in complex acetylene-terminated oligomers[8] that are used in the synthesis of highly temperature-resistant polymers. Since (3-phenoxyphenyl)acetylene possesses a substituent present in the oligomers as well as a reactivity comparable to phenylacetylene,[9] it represents a useful model compound to examine in order to gain insight into the mechanism of polymerization of the acetylene-terminated oligomers. In this paper, we wish to report the kinetics of the bulk polymerization of (3-phenoxyphenyl)acetylene and discuss the mechanistic implications.

Experimental Section

The monomer was obtained from Midwest Research Institute and was purified by vacuum distillation prior to use. Analysis by IR spectroscopy and gel permeation chromatography (GPC) indicated that the monomer purity exceeded 99%.

For kinetic runs, conversion data were determined from isothermal and dynamic differential scanning calorimetry (DSC) measurements, using a Perkin-Elmer DSC-II calibrated against lead and indium at heating rates of 80, 40, 20, 10, and 5 K/min.

0024-9297/79/2212-0895$01.00/0