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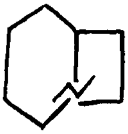
ABSTRACT

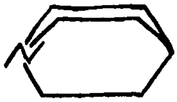
The comprehensive polymerization mechanism of the nitrogen-containing cycles 1-azobicyclo(3,1,0)-hexane (ABH), conidine, quinuclidine, and triethylenediamine under the action of quaternary ammonium salts, ammonium salts, and BF_3 complex with conidine is studied. Polymerization is of the living polymers type, and the active centers of monomer polymerization are ions and ion pairs: the activity of the latter is comparable to and exceeds that of the free ions. The effects of the nature of the counterion, cation, and medium polarity on the reaction rate are investigated. The polymerization rate is found to depend on the nature of the counterion in the polymerization of ion pairs, but not to depend on the counterion in the polymerization of free ions. The reaction rate is proportional to the counterion size in the polymerization of ion pairs. In the case of conidine $K_+ = 0.2$, $K_{\mp}(Cl^-) = 0.28$, $K_{\mp}(Br^-) = 0.36$, $K_{\mp}(I^-) = 0.51$, and $K_{\mp}(ClO_4^-) = 0.62$ (liter)/(mole)(min). The heats of nitrogen-cyclic polymerization are measured and correlated with the activation energy.

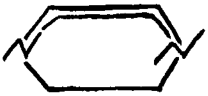
INTRODUCTION

Polymerization of the following nitrogen-containing cycles was studied: conidine [1-azobicyclo(4,2,0)-octane], ABH [1-azobicyclo (3,1,0)-hexane], quinuclidine [1-azobicyclo(2,2,2)-octane], and triethylenediamine [1,4-diazobicyclo(2,2,2)-octane].


ABH


Conidine


Quinuclidine


Triethylenediamine

Monomer selection was due to the following.

1. Synthesis of new polyamines which can be used as ion-exchange resins, films, membranes, polymer catalysts, and physiologically-active compounds.
2. Exclusion of chain transfer to polymer and polymer branching in all monomers contained the tertiary nitrogen atom.
3. Different cyclic strains.
4. The comparative availability of the basic initial compounds for monomer synthesis.

At present there are no papers on the polymerization mechanism of nitrogen-containing cyclics except ethyleneamine. This can possibly be explained by the comparatively minor availability of monomers capable of polymerization. It is apparent from different reports that conidine [1, 2] can polymerize under the action of boron trifluoride and methyl iodide at room temperature, and triethylenediamine [3] can polymerize with acid-type catalysts at temperatures higher than 180°C. Data on quinuclidine and ABH polymerization are absent.

EXPERIMENT

Compounds

The synthesis of conidine, quinuclidine, and ABH was performed according to the experimental technique described earlier [1, 4, 5]. Triethylenediamine from Schuchrdt Co. was used after preliminary sublimation.

Catalysts

Quaternary Ammonium Monomer Salts (QAS)

Monomer (conidine, quinuclidine, triethylenediamine) 0.01 mole and ethyl haloid (iodide, bromide, chloride) 0.01 mole in 25 ml of ether were left at room temperature for several hours. The precipitate was filtered off and washed with ether several times, then dried in vacuum and kept over phosphorus pentoxide.

Quaternary Ammonium Bases (QAB)

These were prepared as follows: Monomer QAS methanol solution was shaken with an excess of silver oxide and filtered off the precipitated silver halide and silver oxide residue. QAS with perchloric anion was obtained from QAB under the action of perchloric acid. Purification was by the above-described procedure.

Ammonium Salts

The preparation of ammonium salts was by the reaction of the monomer with hydrohaloid acids. The salt was precipitated from aqueous solution by acetone, dried in vacuum, and kept over phosphorus pentoxide.

Boron Trifluoride Complex

This complex was obtained by the action of the monomer with an excess of BF_3 etherate in absolute benzene. The BF_3 etherate excess and benzene were removed in vacuum. The complex structure was proved by NMR and elementary analysis. The latter data were: observed (%): H, 7.21; C, 46.10; N, 7.64. Calculated (%): H, 7.14; C, 46.15; N, 7.70.

Solvent

Absolute methanol was obtained by distillation over the Grignard compound. The boiling temperature was 64.5°C.

Methods for the Polymerization Kinetics Study

Thermometrical Method

ABH and conidine polymerization kinetic curves were found by the thermometrical method using a UP-1 instrument. The experimental technique is described in detail in Ref. 6.

Weight Method

Calculated quantities of conidine, ABH, and the catalyst in methanol were sealed in glass ampules and placed in a thermostat held at a certain temperature. After certain time periods the ampoles were broken, and the monomer residue and the solvent were removed in vacuum. After drying in vacuum to constant weight, polymer yield and solution viscosity were determined.

Triethylenediamine and quinuclidine polymerization kinetics were studied both in solution and in bulk by the ampole method. The monomer residue and solvent were removed by washing with ether. Polymer yield and solution viscosity were measured.

Molecular Weight Measurements

Light-Scattering Method

Molecular weights were measured with the CPG instrument of Schimadzu Co. (Japan). Before the intensity of scattered light was measured, the solutions were thoroughly dedusted by filtration through membrane filters of the Millipore Co. (United States) with an average pore diameter of 0.45 μ. Filtration was performed under argon which had been pressure dedusted by consecutive glass filters No. 4 and No. 5. The instrument was calibrated with benzene in thermostatic cells at 25° C. Thermostating was supplied by the circulating water thermostat I-2 with 0.1° C accuracy.

Experimental data analysis of the scattered light intensity measurements was according to Debye [7]. The refractive index increment $\partial n/\partial c$ was measured with the differential refractometer of Schimadzu Co. (Japan) with an accuracy of 4×10^{-3} absolute units in thermostatic cells of 0.5° C accuracy. Measurements were made in polyconidine solution in methanol with concentrations between 0.5 and 1.5%. Polyconidine molecular weight data are given in Table 1.

TABLE 1

Sample	Polymerization conditions	Measurement temperature (°C)	$\partial n/\partial c$	MW
I	Methanol; catalyst N-ethylconidinium iodide, 60° C	25	0.24	15,000
II		25	0.24	25,000
III		25	0.24	65,000

Viscometric Method

Viscosity measurements with a Ubbelohde viscometer were performed for polyconidine in methanol, poly-ABH in benzene, and polytriethylenediamine and polyquinuclidine in concentrated acetic acid. Data on K and α for polyconidine are given in Table 2.

TABLE 2

Sample	Polymerization conditions	MW	$[\eta]$	Constants
I	Methanol; catalyst, N-ethylconidinium iodide, 60°C	15,000	0.19	$K = 2.4 \times 10^{-4}$ $\alpha = 0.7$
II		25,000	0.32	
III		65,000	0.54	

Polymer was separated from the methanol solution by heating in high vacuum.

Polymer elementary analysis data were as follows. Polyconidine: observed %: H, 11.77; C, 75.58; N, 12.55. Calculated %: H, 11.79; C, 75.61; N, 12.60. Poly-ABH: observed %: H, 10.90; C, 72.34; N, 16.78. Calculated %: H, 10.84; C, 72.30; N, 16.74.

Electroconductivity Measurements

The conductivity of catalyst solutions and reaction mixtures in methanol was measured in a cell of the flow type and in a cell with disk electrodes. Platinum electrodes were used in both cases. The cells were thermostated with a circulating thermostat of 0.2°C accuracy. Catalyst solution and reaction mixture conductivities were measured with a conductometer with an operating frequency of 230 Hz. Application of phase detection in the scheme enabled the conductivity active component to be measured. We also used the IKP-type conductometer which provided conductivity measurements with an accuracy of 0.5%. The range of catalysts solution concentration measurements was 10^{-2} to 10^{-5} mole/liter.

Conductivity data are given in Table 3.

TABLE 3

Catalyst	Solvent	λ_∞	K_D
N-ethylconidinium			
chloride	Methanol	102	3.9×10^{-2}
bromide	Methanol	109	2.5×10^{-2}
iodide	Methanol	113	2.4×10^{-2}
iodide	Methanol-dioxane	104	7.8×10^{-5}
perchlorate	Methanol	125	1.4×10^{-2}
Conidinium hydrobromide	Methanol	90	0.8×10^{-3}
Complex BF_3-conidine[a]	Methanol	48	2.0×10^{-3}

[a] λ_∞ and K_D for this system are obviously the effective values because the catalyst is in the following forms: $BF_3CH_3OH + K \rightleftharpoons BF_3K + CH_3OH \rightleftharpoons BF_3OCH_3^{\ominus}, HK^{\oplus} \rightleftharpoons BF_3OCH_3^{\ominus} + HK^{\oplus}$.

RESULTS AND DISCUSSION

Nitrogen-containing cyclic polymerization catalysts were studied. They can be divided into the following groups:

Complexing compounds. Different metal salts capable of complexing can be referred to this group. The polymerization process is caused by both strong Lewis acids (BF_3, $SnCl_4$, $AlCl_3$, $TiCl_4$) and weak ones such as copper, nickel, cadmium, manganese, cobalt halides, nickel nitrates, and also their hydrates. Unlike the oxygen-containing cyclic polymerization catalysts, the nitrogen-containing cyclic polymerization catalysts are the transition metal salts and their hydrates, the latter having the same activity.

Strong organic and inorganic acids. Hydrochloric, hydrobromic, hydroiodic, nitric, perchloric, picric, toluolsulfonic, and trichloracetic acids cause the studied monomers to polymerize. Conidine polymerization, unlike that of quinuclidine and triethylenediamine, is also caused by sulfuric, formic, and phosphoric acids. Acetic acid causes only ABH polymerization.

Organic alkalies of RX-type hydrohalide acids, where R = CH_3, C_2H_5, C_4H_9; X = Cl^-, Br^-, I^-.

Ammonium salts and quaternary ammonium salts (QAS) with different anions (Cl^-, Br^-, I^-, ClO_4^-, $CH_3SO_4^-$, $C_6H_5O^-$).

Monomer complexes with Lewis acids: conidine-BF_3.

Compounds complexing with charge transfer: tetracyanethylene and tetracyanquinodimethane.

Radical and anionic (alkali, amines, etc.) catalysts do not cause nitrogen-containing cyclic polymerization. Thus these cyclics polymerize only by a cationic mechanism.

The kinetics and mechanism of cyclic polymerization were studied for three catalysts groups—ammonium salts (AS), QAS, and the BF_3-monomer complex. Strong inorganic acids and alkyl halides rapidly react with monomers to produce AS and QAS of monomers, which then participate in the reaction. The complete coinciding of all kinetic characteristics proves this. The use of QAS and AS enables the range of catalysts to be expanded and the role of a counterion to be observed more completely.

Methanol and its mixture with dioxane were used as solvents. The use of these solvents made it possible to carry out the reaction under homogeneous conditions.

In order to study the conidine and ABH polymerization kinetics, thermometric and weight methods [6] were used. The results obtained by these two methods are in a good agreement. Quinuclidine and triethylenediamine polymerization kinetic curves were obtained only by the weight method.

Molecular weight was measured by the light-scattering technique in methanol. The degree of polymerization was estimated from the polymer intrinsic viscosity (methanol, 25°C) measured with a Ubbelohde viscometer. We determined the constants of the Mark-Houwink-Kun equation for polyconidine ($K = 2.4 \times 10^{-4}$, $\alpha = 0.7$).

Polymerization under the Action of QAS

The kinetic dependencies of nitrogen-containing cyclic polymerization under the action of QAS are rather simple—there is first order in the monomer, first order in the catalyst, and first order in the reaction. Molecular weights increase proportionally to the degree of conversion, and the slope is always equal to the reciprocal catalyst concentration, independent of the temperature, monomer concentration, and the nature of the counterion (Fig. 1). These data demonstrate fast initiation, participation of all catalyst molecules in the formation of active centers, and the absence of chain termination (first order in the reaction).

Another point of agreement with the "living" system is shown by experiments where fresh monomer is added after completion of the process. The reaction starts again at the previous rate and the polymer molecule weight increases.

Thus nitrogen-containing cyclic polymerization under the action of QAS follows the "living" polymers type with rapid initiation. On the basis of polymerization kinetics data and the fact that the reaction proceeds at a high rate when quaternary ammonium monomers bases (counterion OH^-) are used as catalysts, it is concluded that polymerization proceeds by the cationic S_N2 mechanism.

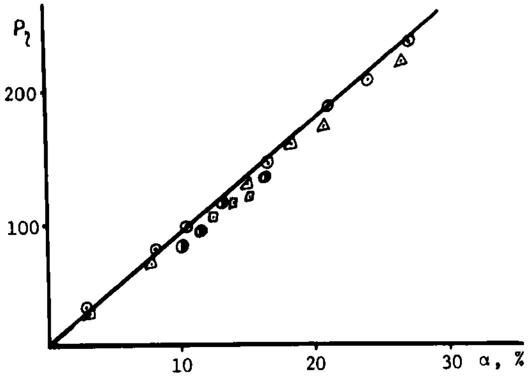


FIG. 1. The degree of polymerization vs of yield of polyconidine under the action of quaternary ammonium salts: ○ N-Ethylconidinium chloride, △, ◑, □ N-Ethylconidinium bromide. Temperature: ○, △ - 60°C, ◑ - 30°C, □ - 40°C. Monomer concentration 6 mole/liter.

Polymerization under the Action of AS and the BF_3 Complex with Conidine

The kinetic dependencies of nitrogen-containing cyclic polymerizations are of a more complicated character if AS, obtained from monomer under the action of inorganic acids, is used, and also if the BF_3 complex with conidine is used as the catalyst.

The pronounced induction period is a specific peculiarity of the kinetic curves of conidine, quinuclidine, and triethylenediamine polymerization on the above catalysts in methanol solution (Figs. 2 and 6). Let us clear up the initiation process kinetic characteristics. The increase of chain numbers with time for different monomer concentrations as well as the rate of polymer chain formation vs monomer concentration are shown in Figs. 3 and 4. It is seen from these figures that the rate of polymer chain formation increases with the initial monomer concentration. The initiation constant is determined from the slope (Fig. 4, left).

The number of chains is calculated by

$$[A^+] = 1.3\alpha[M_0]/\bar{P}_\eta$$

where $\bar{P}_\eta$ is the average viscosity molecular weight and the 1.3 coefficient includes polydispersion of a sample obtained under the

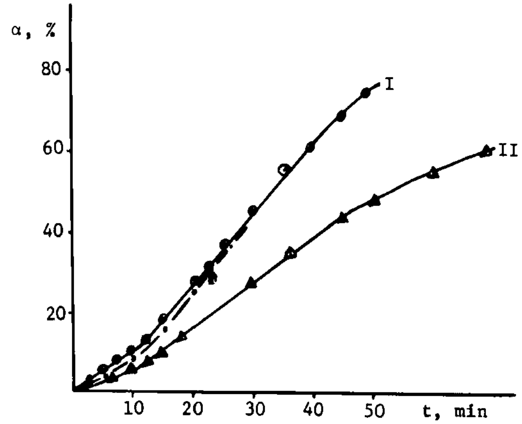


FIG. 2. Experimental curves of conidine polymerization in methanol and the theoretical curve (dashed line) at different catalyst (BF_3 complex with conidine) concentrations. Catalyst concentration: I, 10^{-1} mole/liter, and II, 5×10^{-2} mole/liter. Monomer concentration: 5 mole/liter. Temperature: 60°C.

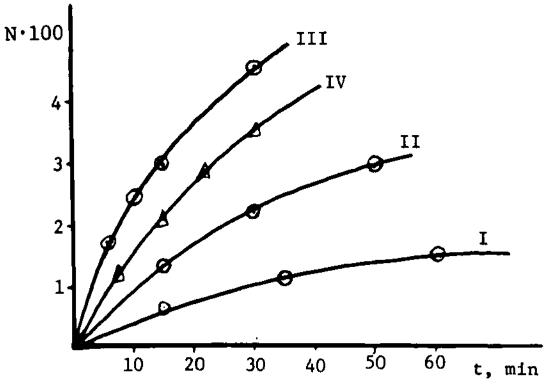


FIG. 3. Number of chains vs reaction time in conidine polymerization under the action of BF_3.conidine and conidinium hydrobromide (IV) at different monomer concentrations: I, 1.5 moles/liter; II, 5 moles/liter; III, 7 moles/liter; and IV, 7 moles/liter. Catalyst concentration: 5×10^{-2} mole/liter. Temperature: 60°C.

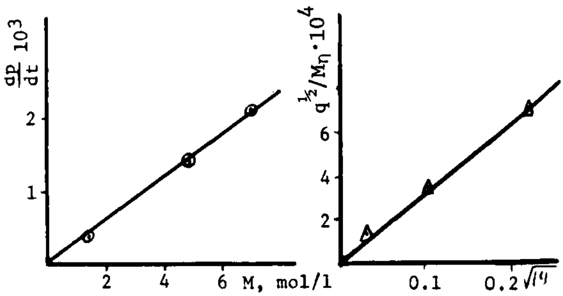


FIG. 4. Active centers formation rate vs conidine initial concentration (left) and molecular weight vs BF_3.conidine complex concentration (right).

conditions of slow constant initiation and the absence of chain termination.

To show that all polymer chains are active in the growth process, the propagation rate constant is calculated with the equation

$$k_p = \omega/[M][A^+]$$

where ω is the current reaction rate determined by graphical differentiation of the kinetic curve.

The propagation rate constant values are given in Table 4. It is seen from this table that the constant calculated in this way does not change with time and coincides with the propagation constant obtained for polymerization under QAS action with the same counterion (Br^-). These data show that there is no chain termination and that the active center nature is the same for QAS and AS initiation.

In the case where there is no termination of active centers, we have for the slow initiation:

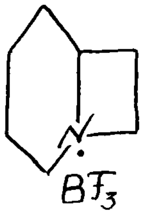
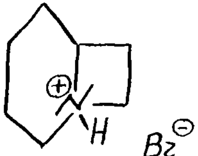
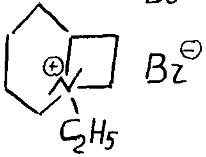
$$I + M \xrightarrow{k_i} A^+$$

$$A^+ + M \xrightarrow{k_p} A^+$$

The kinetic scheme estimation gives the following expression for the active centers concentration in the early reaction stages:

$$[A^+] = \sqrt{\frac{2\,k_i[M_0][I_0]q}{k_p}} \tag{1}$$

TABLE 4. Propagation Rate Constants for Different Types of Initiation

Catalyst	Catalyst concentration (mole/liter)	Monomer concentration (mole/liter)	Reaction time (min)	k_p $\left[\frac{\text{liter}}{(\text{mole})(\text{min})}\right]$	Chain number
	5×10^{-2}	7	6	0.65	0.018
	5×10^{-2}	7	15	0.64	0.030
	5×10^{-2}	7	30	0.62	0.045
	10^{-2}	7	15	0.37	0.0072
	10^{-2}	7	25	0.36	0.008
	10^{-2}	7	46	0.36	0.009
	5×10^{-3}	7	60	0.27	0.004
	5×10^{-3}	7	150	0.29	0.0045
	5×10^{-3}	7	330	0.27	0.0049
	6×10^{-2}	7	15	0.4	0.024
	6×10^{-2}	7	30	0.37	0.038
	6×10^{-2}	7	55	0.38	0.047
	10^{-2}	7	25	0.31	0.008
	10^{-2}	7	40	0.29	0.0082
	10^{-2}	7	90	0.31	0.0095
	6×10^{-2}	6		0.36	
	10^{-2}	6		0.29	
	10^{-3}	6		0.21	

and for the average-number molecular weight:

$$\overline{P}_n = \frac{[M_0]q}{[A^+]} = \sqrt{\frac{k_p[M_0]q}{2k_i[I_0]}} \qquad (2)$$

where $[M_0]$ and $[I_0]$ are the initial monomer and catalyst concentrations, respectively, k_p and k_i are the propagation and initiation rate constants, respectively, and q is the degree of reaction completion.

Thus the number of active centers according to Eq. (1) is proportional to the square root of the degree of reaction completion. The increase of polymer molecular weight is in accord with the same law. Molecular weight vs q for different catalyst concentrations is given in Fig. 5. It is seen from Fig. 5 that there is a linear relationship between polymer molecular weight and the square root of the degree of reaction completion, the slope of the straight lines being a function of catalyst and monomer concentrations, as might be expected by taking Eq. (2) into consideration.

Experimental data according to Eq. (2) for $(q)^{1/2}/\overline{M}_\eta$ and $[I_0]^{1/2}$ coordinates are given graphically in Figs. 4 and 5. The points are quite satisfactorily on a straight line which passes through the origin.

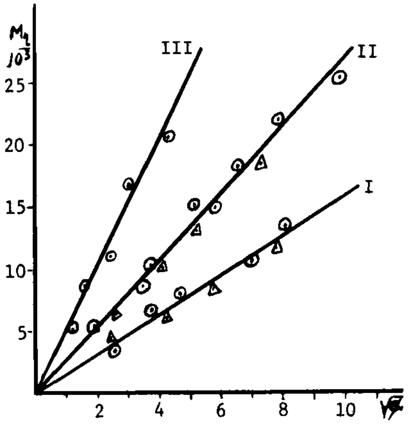
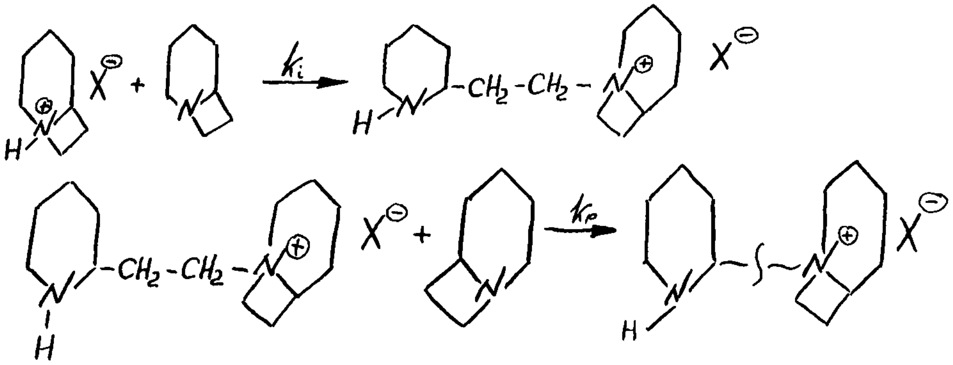


FIG. 5. Molecular weight vs degree of conversion at different catalyst concentrations: I, 5×10^{-2} mole/liter; II, 10^{-2} mole/liter; III, 10^{-3} mole/liter. Conidine concentration: 7 moles/liter, (⊙) BF_3.conidine complex, and (△) conidinium hydrobromide. Temperature: 60° C.

Consideration of the molecular weight regularities of conidine homogeneous polymerization on AS and boron trifluoride complex with conidine leads to the conclusion that, as in the case of QAS polymerization, the above polymerization processes result in "living" polymer systems under the slow initiation conditions. The polymerization process on AS and the complex can be described by



Experimental data on triethylenediamine, quinuclidine, and ABH polymerization studies are in a good agreement with the above results. Thus, in the cases of triethylenediamine and quinuclidine polymerization under AS action, an induction period is observed (Fig. 6); when using monomers of QAS as catalysts, an induction period is absent. It follows from Fig. 6 that triethylenediamine and quinuclidine polymerization rates differ by a factor of 2. Thus the monomers activities are equal because triethylenediamine has two nitrogen atoms.

Structure of Active Centers

One of the basic questions of cationic polymerization is the nature of the active centers.

At present the ion and ion pairs concept is assumed for most systems. As a demonstration of ion and ion pairs existence in nitrogen-containing cyclic polymerization, conductivity measurements of polymerization and catalytic systems in methanol were performed. Conductivity study of catalyst solutions in methanol enabled a degree of ion pairs dissociation to be evaluated at different salt concentrations, the ion pairs dissociation constant to be determined.

A monomer addition of 2 to 4 moles/liter has little effect on the conductivity value. The latter is not affected much in the course of

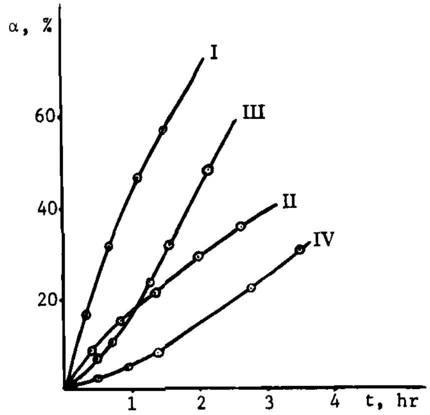


FIG. 6. Kinetic curves of triethylenediamine (I, III) and quinuclidine (II, IV) polymerization under the action of quaternary ammonium salts (I, II),and ammonium salts (III, IV). Catalysts (iodides) concentration: 10^{-2} mole/liter. Monomer concentration: 8.5 mole/liter. Temperature: 195°C.

polymerization, decreasing slightly, obviously, due to the viscosity increase and the ionic mobility decrease, which shows the validity of extrapolating the data obtained for catalysts in methanol to the polymerization system.

It follows from our data that all the catalysts studied have high conductivity in methanol. The boron trifluoride complex with conidine is not excluded in this case.

The existence of free ions has thus been proved, and their quantity and dissociation constant have been measured.

From the polymerization kinetics and conductivity data, the effective rate constant vs degree of dissociation is drawn (Fig. 7). The linear relationship between the degree of dissociation and the effective propagation rate constant is seen for different catalysts. This is the first evidence that ions and ion pairs are the active centers. The dependence of the propagation rate constant on the degree of salt dissociation at $\alpha \to 0$ converges to a point, i.e., the polymerization rate is independent of the counterion for all observed catalysts when the ion pairs dissociation is complete (polymerization on the free ions). This is the second basic proof of ion and ion pairs participation in the propagation process. Notice that ion pairs are more active than free ions.

The third decisive argument for ion and ion pairs participation in the chain propagation process (namely of those ions which are

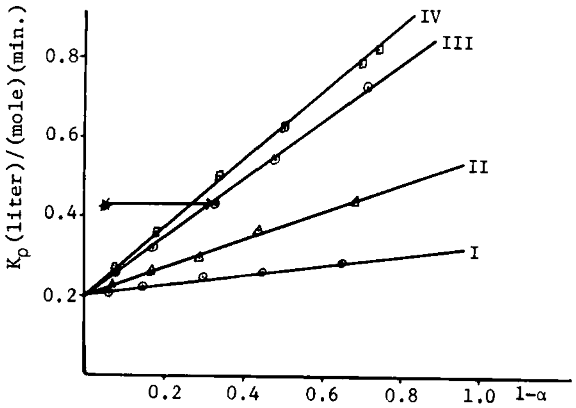


FIG. 7. Propagation rate constant of conidine polymerization vs degree of salt dissociation. I, N-Ethylconidinium chloride; II, bromide; III, iodide; and IV, perchlorate. CsI salt (10^{-2} mole/liter) was added. The arrow shows the degree of dissociation corresponding to this concentration. Monomer concentration: 6 moles/liter. Temperature: 60°C.

responsible for the conductivity of catalytic and polymerization systems) is the action of neutral salt additions. In case ions are really the active centers, neutral salt addition should suppress ion pairs dissociation, shifting the equilibrium to the ion pairs and changing the polymerization rate.

CsI (10^{-2} mole/liter) was added to the polymerization system catalyzed by N-ethyl conidinium chloride (concentration 10^{-3} mole/liter); only free ions were present in the system (see the conductivity data). The polymerization rate increased while the equilibrium shifted to the ion pairs. At the same time, addition of CsCl (10^{-2} mole/liter) to the system catalyzed by N-ethylconidinium iodide did not change the reaction rate as the activities of ion pairs and free ions were found to be practically equal in the case of Cl^- counterions.

In a similar way it is possible to elucidate the role of ions and ion pairs in the initiation process. The initiation rate constant vs the degree of ammonium salt dissociation is given in Fig. 8. It is seen from this figure that the initiation rate constant increases similarly to the propagation rate constant, i.e., with a decrease of the degree of salt dissociation.

Thus the initiation and propagation reactions proceed similarly. Nevertheless the rate constants of these reactions differ by 2 to 3 orders. An analogy may be drawn here with the oxygen-containing cyclics. In dioxalane, trioxane, and tetrahydrofurane polymerization under the action

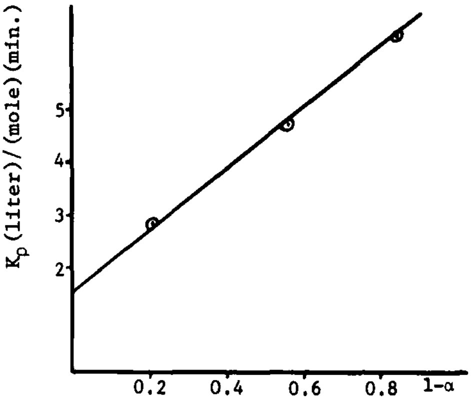


FIG. 8. Initiation rate constant of conidine polymerization vs degree of BF_3.conidine complex dissociation. Monomer concentration: 5 moles/liter. Temperature: 60°C.

of oxonium salts and other cationic catalysts, water influences polymerization as an inhibitor. It is supposed that the less active secondary oxonium ion is formed as a result of the tertiary oxonium ion reaction with water:

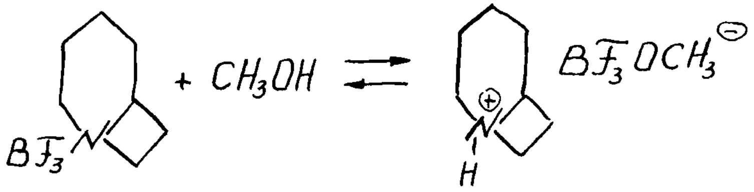
$$R_3O^+ + H_2O \rightarrow R_2O^{\oplus} H + ROH$$

The results obtained demonstrate that onium ions of the R_3HN^+ type (identical with R_2HO^+) react with monomer much slower than the ions of the R_4N^+ type (identical with R_3O^+). This is true for active centers both in the form of free ions and ion pairs.

The reduced AS activity in comparison with QAS in the initiation reaction can be explained by two effects:

1. Steric repulsion tensions in alkyl groups result in the fact that the C—N bond energy in QAS is less than in AS and therefore the first bond breaks easier.
2. The tertiary ion is better solvated and the solvation energy partial loss thus occurs during the initiation reaction.

In most kinetic studies relating to cationic polymerization of oxygen-containing cyclics, boron trifluoride is used as a catalyst. It should be noticed that the mechanism of initiation by this catalyst of the oxygen-containing cyclic polymerization is not yet elucidated. A correlation of kinetic (existence of an induction period; molecular weight growth proportional to the square root of the degree of reaction completion and initiator and monomer initial concentrations; reaction rate constants on the free ions have the same values with AS and QAS) and conductivity data for conidinium hydrobromide and the BF_3 complex with conidine enables one to assume that their active centers structures are similar and that the active center formation procedes according to the scheme



The slow initiation observed in this system is an argument for such a cation structure, and the high conductivity is an indication of the formation of a strongly dissociating salt product. Direct proof of the active center structure is obtained by NMR spectroscopy. The cation structure is demonstrated by a comparison of the proton spectra of the BF_3 complex and conidine AS in methanol. The spectra of these systems are identical (Fig. 9), which points to the same cation nature in both cases. The anion structure is ascertained by a spectra study of ^{19}F and ^{11}B in methanol and their comparison with the model system spectra ($KOCH_3.BF_3$ salt in methanol) (Fig. 10). A correlation between the complex, oligomer, and model compounds in methanol NMR spectra parameters indicates conclusively that the proposed mechanism of the active center formation is favorable.

Counterion, Cation, and Medium Influence

An idea about the growing chain being an ion pair raises a consideration of the counterion influence on the chain propagation rate.

We especially studied the influence of the counterion nature on the polymerization kinetics of conidine, ABH, quinuclidine, and triethylenediamine. Monomer QAS with different counterions was used as the catalyst.

Conductivity measurement of the catalyst solutions in methanol enabled a degree of QAS, AS, and BF_3 complex with conidine dissociation to be evaluated at different concentrations, and the equivalent conductivities and ion pairs dissociation constants to be determined.

Notice that in this case there obviously exist only contact ion pairs because the formation of solvent-separated ion pairs in the

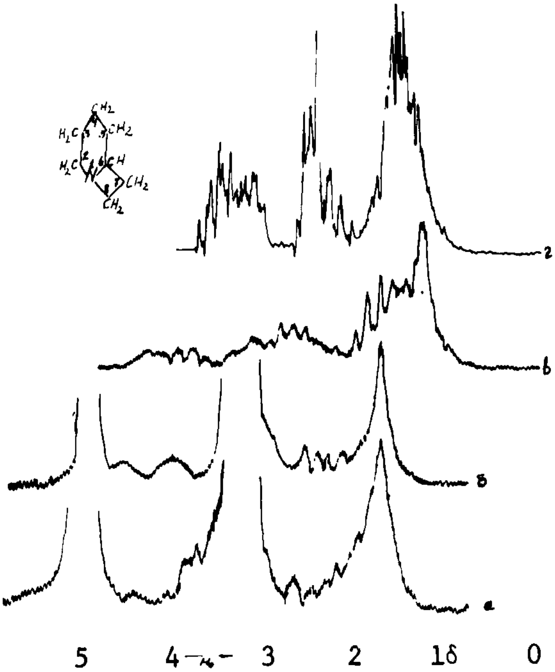


FIG. 9. NMR spectra on ^1H nuclei: (a) conidine-hydrobromide (1:1) in methanol; (b) BF_3.conidine complex in methanol; (c) BF_3.conidine complex in benzene; and (d) conidine in benzene. Temperature: 25°C.

presence of large and inadequately solvated ions is highly improbable. It is seen from the dependence of the propagation rate effective constant on the degree of salt dissociation as given in Fig. 7 that the polymerization rate is a function of the counterion nature in the case of the polymerization on ion pairs and is independent of the counterion in the case of the polymerization on free ions.

It should be especially pointed out that if in the anionic polymerization of vinyl monomers the free ion activity exceeds that of the ion pairs, then in conidine polymerization the observed ion activity is comparable to or even below that of the ion pairs. This can be explained by the following facts. Counterion influence on the polymerization rate shows up in two ways. On the one hand a counterion shields the active center and there is a necessity of a partial dissociation of the ion pair in the transient state in the course of monomer addition to the active center which should require additional energy. On the

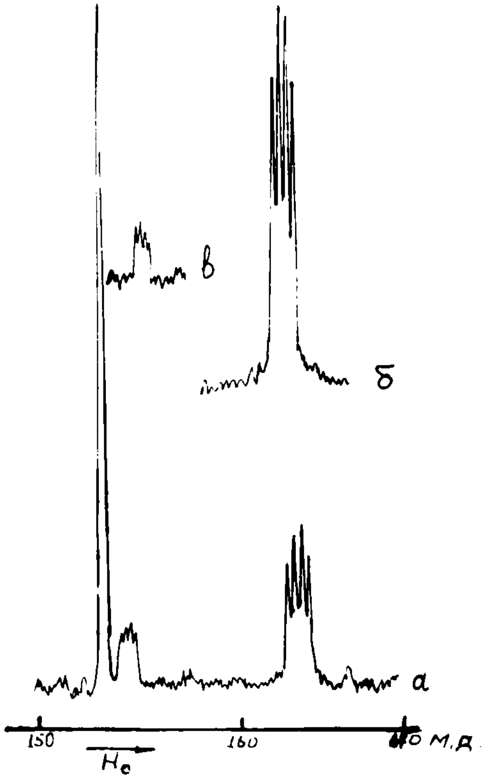


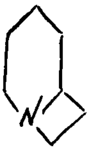
FIG. 10. NMR spectra on ^{19}F nuclei: (α) BF_3.conidine complex in methanol; (β) BF_3.conidine complex in benzene; (δ) $K^+BF_3OCH_3^-$ in methanol. Temperature: 35°C. $CFCl_3$ external standard.

other hand a counterion stimulates additional monomer polarization by a "push-pull" mechanism.

In the case of the anionic polymerization of vinyl monomers, a counterion in contact with a ion pair is in the vicinity of the carbanion and their interaction is essential.

The cationic polymerization of nitrogen-containing cyclics (and probably also oxygen-containing cyclics) is quite different. For one thing the size of the active center (ammonium or oxonium cation) is much larger and thus its interaction with a counterion is essentially weaker. For another, monomer attacks the α-carbon atom of a four-membered cyclic instead of the nitrogen atom bearing the main charge. In such a case it is possible that a transient cyclic complex configuration (an anion being a part of it) is convenient for the "push-pull" mechanism.

TABLE 5

Monomer	Catalyst	Catalyst concentration (mole/liter)	k_p [(liter)/(mole)(min)]
Conidine 	N-ethylconidinium		
	chloride	6×10^{-2}	0.28
	bromide	6×10^{-2}	0.36
	iodide	6×10^{-2}	0.51
	perchlorate	6×10^{-2}	0.62
	BF_3.conidine	6×10^{-2}	0.63
		10^{-2}	0.48
		5×10^{-3}	0.29
	Conidinium hydrobromide	6×10^{-2}	0.38
	N-ethylconidinium iodide	6×10^{-2}	0.59
		5×10^{-3}	0.48
	Free ions		0.2
A B H 	N-ethylconidinium		
	chloride	5×10^{-2}	1.1
	perchlorate	5×10^{-2}	6.3
	N-methylconidinium methylsulfate	5×10^{-2}	7.2
	Ethyl iodide	5×10^{-2}	2.6
	BF_3.ABH	5×10^{-2}	5.7
	Free ions		2.7
Triethylene-diamine		2×10^{-1}	0.5
		2×10^{-3}	0.125
Quinuclidine		2×10^{-2}	

k_i [(liter/ (mole)(min)]	ΔH (kcal/ mole)	E (kcal/ mole)	Log A [(liter/ (mole)(min)]	Ion τ (A°)	Note
	16.8	14.9	9.1	1.81	60°C
		13.8	8.5	1.96	60°C
		12.2	7.7	2.16	60°C
		11.9	7.4	2.36	60°C
0.0065					60°C
0.0047					60°C
0.0028					60°C
					60°C
					60°C Solvent methanol-dioxane (1:2)
					60°C
		11.4	6.6		60°C
	23.4				40°C
					40°C
					40°C
					40°C
					40°C
		9.1 ± 1			40°C
	2.3 ± 0.5	19.2 ± 1			195°C ΔH_{ss}
	11,2				195°C ΔH_{sc}
	10,5				195°C ΔH_{sc}

The free ion data were obtained at catalyst concentrations of 10^{-3} mole/liter when the ion pairs contribution was small. Other results were obtained at a catalyst concentration of 6×10^{-2} mole/liter when the reaction proceeded on both free ions and ion pairs. The effective activation energy and the preexponential factor of the Arrhenius equation decreased as the counterion radius increased (Table 5).

Experimental data obtained under corresponding conditions for other nitrogen-containing cyclics are in a good agreement with the data of the conidine polymerization study. Some differences in polymerization can be easily explained by the same ideas about nitrogen-containing cyclic structure peculiarities. Thus the three-membered cycle has a smaller size than the four-membered one. The smaller the size of an active complex component (cation and counterion), the more important is the role of the first factor (active center shielding by the counterion). This explains the increase of ion pairs reactivity with counterion size for a given cyclic, and also the lower relative activity of ion pairs with a given counterion for a three-membered cyclic in comparison with a four-membered one (relative to the free ions). In this case it is impossible to compare the absolute activity of three- and four-membered cyclics because they have different strains and basicities.

Data on polymerization rate vs medium polarity in all systems studied show that the reaction rate increases with polarity of the medium. This is quite natural because the activity of free ions is higher than that of ion pairs in these systems.

To check the influence of the polarity of the medium on the reaction rate, conidine polymerization in a methanol-dioxane mixture has been studied. The reaction in this mixture has shown that the reaction rate increases as the dielectric constant of the medium decreases when N-ethylconidinium iodide is used as a catalyst (Table 6).

TABLE 6

Catalyst concentration (mole/liter)	K_p [liter/(mole)(min)]	
	Methanol	Methanol-dioxane (1:2)
10^{-1}	0.68	0.72
6×10^{-2}	0.47	0.58
5×10^{-3}	0.35	0.48

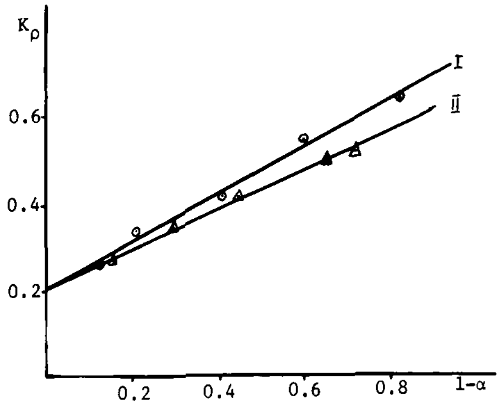


FIG. 11. Propagation rate constant of conidine polymerization vs degree of N-ethylconidinium iodide dissociation in methanol (I), and in methanol-dioxane (1:2) mixture (II). Monomer concentration: 6 moles/liter. Temperature: 60°C.

A decline in the dielectric constant of the medium leads to a decrease in the degree of salt dissociation, and shifts the equilibrium to the ion pairs having higher activity in the given system than the free ions.

The conductivity of N-ethylconidinium iodide salt in a methanol-dioxane mixture was measured and equivalent conductivity and dissociation constants were calculated. The chain propagation rate effective constant vs the degree of salt dissociation in methanol and methanol-dioxane mixture are shown in Fig. 11. As seen from Fig. 11, the propagation rate constant of the free ions is practically independent of the polarity of the medium, and for ion pairs it increases slightly with the dielectric constant of the medium.

The same medium effect upon ions and ion pairs activity is described for styrene and α-methylstyrene anionic polymerization. Yet the reaction rate changes with the dielectric constant medium are opposite in conidine cationic polymerization and vinyl monomers anionic polymerization because the main action of the polarity of the medium change amounts to a change of a degree of ion pairs dissociation, and the relation between ion and ion pairs activities in nitrogen-containing cyclics and vinyl monomer polymerization is the reverse.

Heat of Polymerization

The heat of the polymerization process

M (liquid) $\rightarrow$ P (solution) was measured. The heats of the polymerization reactions are 16.8 kcal/mole for conidine, 23.4 kcal/mole for ABH, and 2.3 kcal/mole for triethylenediamine. The heats of triethylenediamine and quinuclidine polymerization for the process

$$\text{M (liquid)} \rightarrow \text{P (solid)}$$

were also determined. The heats of triethylenediamine and quinuclidine polymerization are 11.2 and 10.5 kcal/mole, respectively. The initial stage of polymerization proceeds under homogeneous conditions, and this allows determination of the polymerization heat for the process

$$\text{M (liquid)} \rightarrow \text{P (solution)}$$

The average value of triethylenediamine polymerization heat is 2.3 ± 0.5 kcal/mole.

Experimental data obtained for nitrogen-containing cyclic polymerization with different cyclic strains permits correlation between the propagation activation energy of the free ions and the heat of polymerization. As with radical reactions, the Polani-Semenov correlation may be written in the linear form:

$$E = A - \alpha \Delta H$$

where $\alpha = 0.52$.

Correlation of the results obtained for the nitrogen-containing cyclic polymerization in methanol with three different groups of catalysts enables conclusions about the unified nature of the active center to be drawn.

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