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Kinetics and Mechanism of the Boron Trichloride Catalyzed Thermal Ring-Opening Polymerization of Hexachlorocyclotriphosphazene in 1,2,4-Trichlorobenzene Solution

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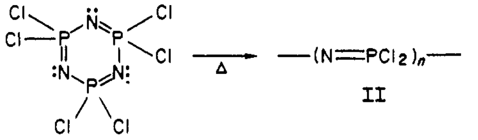
ABSTRACT: The products and kinetics of the boron trichloride (BCl_3) catalyzed thermal ring-opening polymerization of hexachlorocyclotriphosphazene ($(NPCl_2)_3$) have been investigated in 1,2,4-trichlorobenzene solution at 170–230 °C in sealed glass tubes under vacuum. Polymeric products were characterized by high-performance size exclusion chromatography, membrane osmometry, light scattering, and dilute solution viscometry. The BCl_3-catalyzed polymerization is not cocatalyzed by water, but polymerization is strongly inhibited by aryl phosphates. Polymerization rates were determined by monitoring $(NPCl_2)_3$ concentration with laser Raman spectroscopy. The kinetic data fit a mechanism that involves initiation, catalysis, and inhibition of polymerization by BCl_3, depending on the experimental conditions.

Introduction

The thermal ring-opening polymerization of hexachlorocyclotriphosphazene ($(NPCl_2)_3$ (I)) (eq 1) is the principal synthetic route to poly(dichlorophosphazene) (II), which is the precursor to the technologically promising poly(organophosphazenes). Unfortunately, the uncatalyzed polymerization is difficult to control and often produces insoluble, cross-linked polymers at high conversion which are almost useless for preparing the organosubstituted polymers.[1] Variations in chloro polymer characteristics are even observed between different batches of I under the same polymerization conditions. The thermal polymerization has been studied extensively and is reviewed in recent literature.[2] It is generally agreed that the reaction is a cationic chain growth polymerization. The initiation mechanism is frequently proposed to be one of two processes, either ring opening of I or Cl⁻ dissociation from I (eq 2 and 3).[3-5]



I   II   (1)

$$I \rightarrow {}^{-}N{=}(PCl_2N)_2{=}PCl_2^{+} \quad (2)$$

$$I \rightleftharpoons (N_3P_3Cl_5)^{+}\,Cl^{-} \quad (3)$$

A great many compounds have been found to promote the polymerization of I.[2,6,7] Although many catalysts increase the polymerization rate and are effective at promoting polymerization of I at temperatures lower than those required for the uncatalyzed reaction, the majority also enhance the tendency of the reaction to form cross-linked material. Boron trichloride (BCl_3) is an effective catalyst for the reaction, promoting polymerization at temperatures as low as 150 °C to give >80% soluble polymeric II.[8] There have been few kinetic studies of the catalyzed polymerization and none reported for BCl_3.

We have studied the BCl_3-catalyzed thermal solution polymerization of I and propose a mechanism which should

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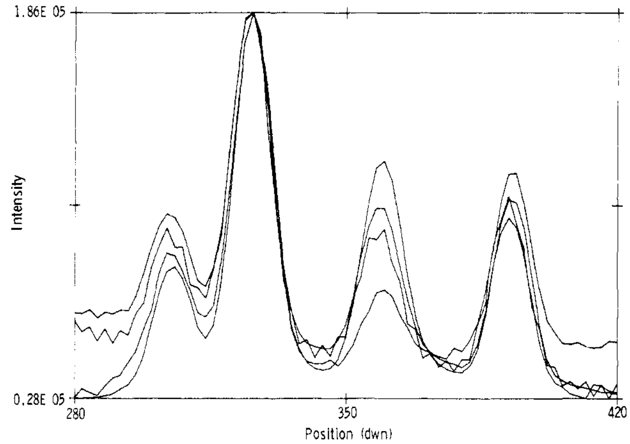


Figure 1. Sequential Raman spectra of polymerizing TCB solution of I. Polymerization temperature 170 °C, $[BCl_3] = 0.16$ *m*, $[I]_0 = 0.54$ *m*. Elapsed time (h:min)/% conversion: 0:00/0, 26:15/18.10, 45:15/42.66, and 83:55/61.03.

be useful in future efforts to optimize and control the polymerization reaction. The solvent 1,2,4-trichlorobenzene (TCB) has a low vapor pressure and resists attack by BCl_3. The concentration of I in polymerizing systems was directly monitored by laser Raman spectroscopy. Polymers II and $(NP(OCH_2CF_3)_2)_n$ (III) (prepared by reaction of II with $NaOCH_2CF_3$) were characterized by high-performance size exclusion chromatography (SEC), light scattering, membrane osmometry, and dilute solution viscosity (DSV) measurements.

Experimental Section

Materials. Toluene and heptane were distilled from CaH_2 under N_2 and stored under N_2. HPLC-grade TCB (Fisher) was saturated with N_2 upon opening, stored under N_2, and used without further purification. HPLC-grade THF (no stabilizer added) was used as received from Burdick and Jackson and stored under helium. The cyclic trimer I (Phosnic 390, Inabata Co., Japan) was purified by repeated recrystallization from heptane followed by sublimation. BCl_3 (99.95%) was used as received from Matheson Gas Products.

Measurements. Polymerizations monitored by Raman spectroscopy were carried out in heavy-walled Pyrex tubes (5 mm o.d. × 200 mm, approximate volume 2 mL). Larger ampules (22 mm o.d. × 220 mm, approximate volume 30 mL) were used to prepare polymers for characterization.

Because of the difficulties involved in determining solution densities and hence molarities, all concentration values are given in units of molality (*m*). Except where specified differently, all polymerizations were carried out with 0.54 *m* solutions of I. In a typical experiment a flame-dried polymerization tube was filled in the drybox with approximately 2 g of a TCB solution of I. The tube was then degassed outside the drybox using a vacuum line and ultrasonic agitation. A measured quantity of BCl_3 was condensed into the tube at 77 K. The tube was then sealed with a flame. Polymerization was carried out in a thermostated aluminum block heater controlled to within 1 °C of the desired temperature.

Laser Raman spectroscopy was performed with a Spex Industries Model 1401 spectrometer coupled to a Spex Datamate system and a Spectra-Physics 2-W argon ion laser. The initial Raman spectrum of the solution of I was recorded at room temperature from 280 to 420 cm^{-1} (Figure 1). The sample was then heated to polymerization temperature. The reaction was halted at intervals by removing the tube from the heat source and cooling to room temperature. The Raman spectrum of the sample was then measured. Peak areas at 327 and 361 cm^{-1} (due to TCB and I, respectively) were calculated and the ratio of the peak areas (A_{361}/A_{327}) was used to determine the concentration of I (Figure 1). The calibration curves were linear for 0.05–0.54 *m* solutions of I in TCB.

Polymer samples II prepared in large ampules were characterized by SEC and DSV and then reacted with THF solutions of $NaOCH_2CF_3$ in the drybox at room temperature to produce the stable polymer III for further characterization by light scattering and membrane osmometry.[9]

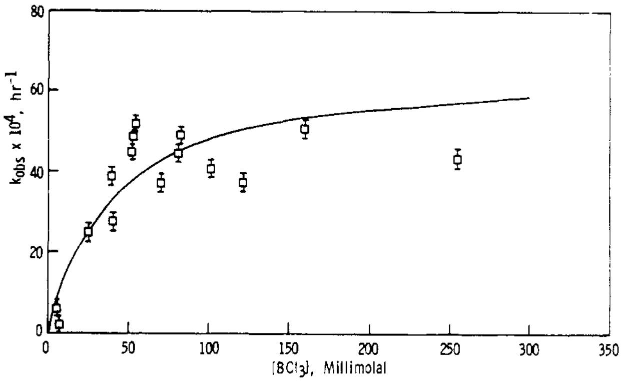


Figure 2. Dependence of the observed rate constant, k_{obsd}, on BCl_3 concentration over the region of low $[BCl_3]$ at 170 °C and $[I]_0 = 0.54$ *m*. Calculated curve is based on parameters in the proposed mechanism.

Table I
Chromatographic Parameters

sample concentration	0.5% (w/v)
injection volume	200 μL
mobile phase	THF
flow rate	1 mL/min
columns	Jordi GPC-Gel mixed bed

Size exclusion chromatography with THF as the mobile phase was carried out on a Waters 244 ALC/GPC instrument with a 6000A solvent delivery system, a U6K injector, and an R400 refractive index (RI) detector coupled to a Spectra-Physics SP4000 data system. Additional chromatography was performed on a Waters 150 ALC/GPC instrument coupled to a Waters Data Module.[10] Table I details the chromatographic conditions.

Light scattering measurements were performed on a Fica Model 50 instrument with $\lambda_0 = 546.1$ nm and $dn/dc = -0.027$ mL/g for THF solutions of III.[10]

Membrane osmometry measurements were made on a Hewlett-Packard Mechrolab Model 501 high-speed membrane osmometer equipped with an Arro Laboratories Type 600 cellulose acetate membrane.

Dilute solution viscosity measurements were made with Cannon Ubbelohde type viscometers immersed with a 40-L water bath controlled to within 0.1 °C of the desired temperature. Polymer II was analyzed in TCB solution at 41 °C by diluting 1.0 g of the polymerization solution (including all reaction products) to 10 mL in a volumetric flask. The polymer concentration determined was based on the concentration of unreacted I. Polymer III was separated from low molecular weight products by precipitation and analyzed in THF solution at 25 °C.

Results

Reaction Rates. Plots of log $([I]/[I]_0)$ vs. time (where $[I]_0$ and $[I]$ are the initial and instantaneous concentrations of I, respectively) were linear for at least one half-life at constant temperature and $[BCl_3]$. This indicated first-order polymerization, eq 4, where k_{obsd} is the observed

$$-d[I]/dt = k_{obsd}[I] \qquad (4)$$

first-order rate constant. This reaction order is to be expected, since consumption of I is due almost entirely to propagation at low $[BCl_3]$ and the concentration of growing chain ends is much lower than [I]. Stopping and starting the reaction repeatedly by removing the heat source had no effect on the overall rate of reaction at fixed temperature.

The variation of k_{obsd} with $[BCl_3]$ at 170 °C and $[I] = 0.54$ *m* is shown in Figure 2. After an initial sharp increase, k_{obsd} reaches a plateau and is apparently independent of BCl_3 concentration over the interval 0.05 *m* <

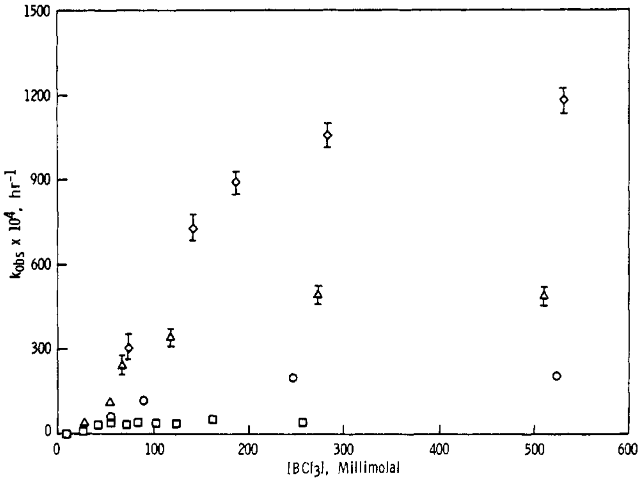


Figure 3. Dependence of k_{obsd} on [BCl_3] at 170 (□), 190 (○), 210 (△), and 230 °C (◇) at $[I]_0 = 0.54$ *m*.

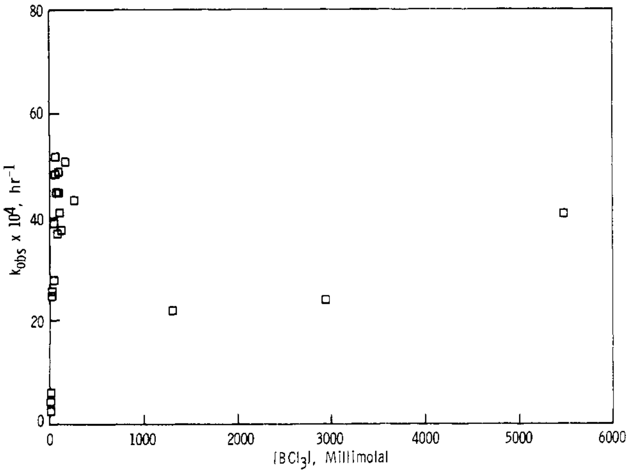


Figure 4. Dependence of k_{obsd} on [BCl_3] at 170 °C and $[I]_0 = 0.54$ *m*, showing the effect of high [BCl_3].

Table II
Dependence of $\bar{M}_w$ on Extent of Conversion[a]

sample	% conversion	$\bar{M}_w$
1	5.1	8400
2	20.2	18000
3	35.0	26000

[a] TCB solution polymerization. [BCl_3] = 2.7×10^{-2} *m*, $[I]_0$ = 1.06 *m*. Relative molecular weights of poly(dichlorophosphazene) by SEC based on polystyrene standards.

[BCl_3] < 0.50 *m*. Stopping the reaction and removing BCl_3 (under vacuum at room temperature) always caused a sharp decrease in the rate when polymerization was resumed. Similar dependences of k_{obsd} on [BCl_3] were observed over the temperature range investigated (Figure 3). Figure 4 shows that, at 170 °C and 0.54 *m* I, k_{obsd} decreases sharply when [BCl_3] = 0.5–1.0 *m* and then slowly increases with increasing BCl_3 concentration from 1.5 to 5.0 *m*. The origins of these effects are discussed in the following sections.

Molecular Weights. Analysis of II by SEC during the course of a reaction showed that the molecular weight of the polymer increased steadily as a function of conversion. Typical results shown in Table II suggest that there is no termination step in the BCl_3-catalyzed polymerization of I. The molecular weight distribution of the polymeric product is more symmetrical than that of an uncatalyzed polymerization (Figure 5), suggesting that one BCl_3-catalyzed polymerization mechanism is operative under these conditions. Figure 6 shows the dependence of the inherent viscosity of III on [BCl_3] at 190 °C and $[I]_0 = 0.54$ *m*. All polymers were products of reactions carried to 60% conversion. The maximum observed at [BCl_3] = 0.17 *m* corresponds to the point at which k_{obsd} becomes independent of [BCl_3] at 190 °C (Figure 3). No high polymer was formed at [BCl_3] > 5.0 *m*; only low molecular weight oligomers were detected by SEC. The inherent viscosity of III increased as the temperature was increased from 170 to 230 °C at constant [BCl_3] and $[I]_0$ (Figure 7).

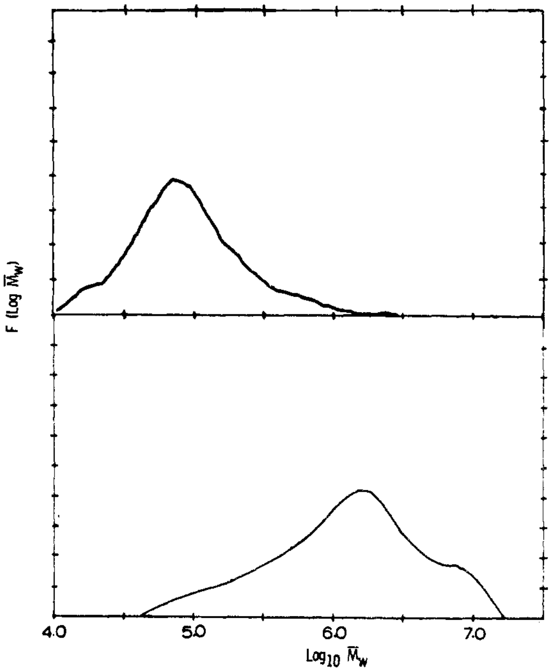


Figure 5. Comparison of polymer molecular weight distributions (determined by SEC) of polymers from (top) catalyzed polymerization and (bottom) uncatalyzed polymerization.

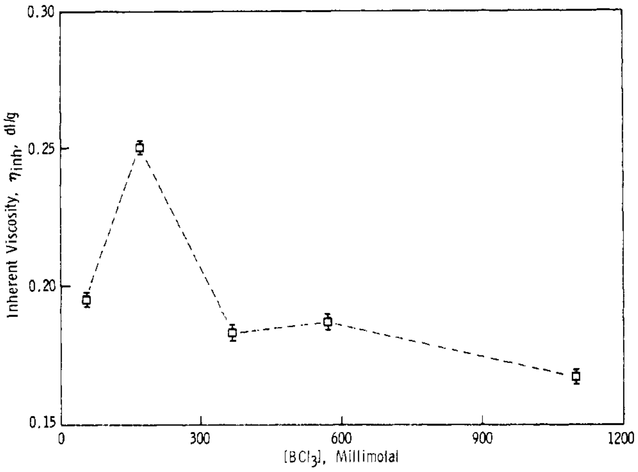


Figure 6. Dependence of the inherent viscosity of III on [BCl_3]. Polymers prepared at 190 °C and 0.54 *m* $[I]_0$ in reactions carried to 60% conversion.

Effect of H_2O. It has been observed in the uncatalyzed melt polymerization of I that the presence of small amounts of water can accelerate the reaction and tends to promote cross-linking,[11] suggesting that water acts as either a catalyst or a cocatalyst for polymerization. Water was added to BCl_3-catalyzed polymerization reactions in concentrations varying from $<3 \times 10^{-5}$ to 0.17 *m*. Trace amounts of water had no apparent effect on the reaction, while larger amounts lowered the rate of reaction, presumably by forming $B(OH)_3$, which is catalytically inactive.

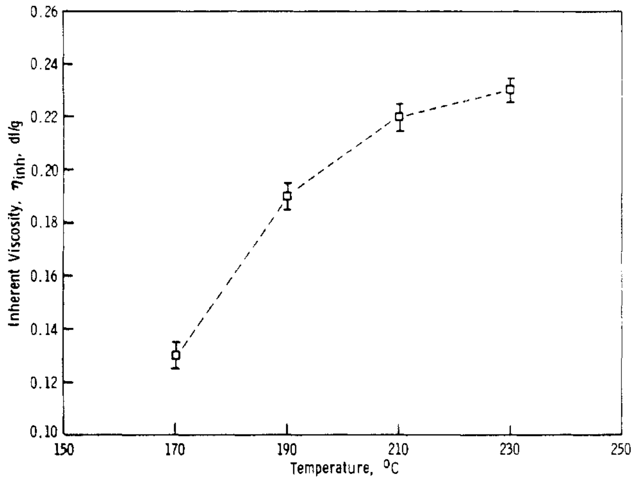


Figure 7. Dependence of the inherent viscosity of III on polymerization temperature at $[BCl_3] = [I]_0 = 0.54$ *m*. Polymerizations carried to 60% conversion.

Clearly, water is not important as a catalyst or cocatalyst in the BCl_3-catalyzed polymerization of I.

Effect of $(RO)_3PO$. The role of organophosphates in the thermal polymerization of I was investigated because $(RO)_3POBCl_3$ was reported to be an effective catalyst for the reaction.[12] It was found that triphenyl phosphate acted as a powerful polymerization inhibitor. Thus I was recovered unchanged after 300 h from an attempted melt polymerization with 0.42 mol % of $(C_6H_5O)_3PO$ at 225 °C, while 40% conversion to II was observed after 100 h without phosphate present. Other aryl phosphates also were found to inhibit polymerization. It has been reported that other Lewis bases inhibit the melt polymerization of I at 220 °C,[7] including Dabco (1,4-diazabicyclo[2.2.2]octane), urea, and triphenylphosphine. The degree of inhibition was a function of basicity; e.g., urea inhibited polymerization only above 6 mol % concentration whereas Dabco was an effective inhibitor at 1 mol %.[7] These observations support the proposal of a cationic center as the site of propagation.

Mechanistic Proposals. Initiation. Possible mechanisms of catalyzed initiation and structures of the polymer chain end are proposed below.

Ring Opening

$$2BCl_3 + (N_3P_3Cl_6) \rightarrow \underset{IV}{Cl_2B\text{-}(N{=}PCl_2)_2\text{-}N{=}PCl_2{}^+BCl_4{}^-} \rightarrow Cl_2B\text{-}(N{=}PCl_2)_5\text{-}N{=}PCl_2{}^+BCl_4{}^- \quad (5)$$

Chloride Abstraction

$$BCl_3 + (N_3P_3Cl_6) \rightleftharpoons (N_3P_3Cl_5)^+BCl_4{}^- \rightarrow (N_3P_3Cl_5)\text{-}(N{=}PCl_2)_2\text{-}N{=}PCl_2{}^+BCl_4{}^- \quad (6)$$

Mechanisms 5 and 6 are derivatives of the mechanisms proposed for the uncatalyzed thermal polymerization of I. Mechanism 5 is supported by the work of Moran,[13] who reacted PCl_5 and I at 250 °C in vacuo and obtained a compound he proposed as V based on ^{31}P NMR data and

$$\underset{V}{Cl_3P{=}(NPCl_2)_2{=}NPCl_3{}^+PCl_6{}^-}$$

elemental analysis. Moran was able to substitute $BCl_4{}^-$ for $PCl_6{}^-$ in V by bubbling BCl_3 gas through a benzene solution of V. Based on these findings it seems possible that BCl_3 reacts with I in a fashion similar to mechanism 5. Attempts to identify a compound such as IV in the products of reactions of I with large excesses of BCl_3 have been unsuccessful.

Direct study of the initiation reaction is difficult since initiation only accounts for a small fraction of I being consumed. Inducing initiation in the absence of propagation is not routinely possible for polymerizing systems. However, it appears that initiation can be isolated in the BCl_3-catalyzed polymerization of I. High polymer is not formed at very high BCl_3 concentrations and 170 °C and the only products are very low molecular weight oligomers. This observation is not surprising as one expects more chains to be initiated as the catalyst concentration is increased. What is unusual is that the overall rate of consumption of I decreased at high BCl_3 concentrations (Figure 4). These observations together suggest that propagation is being inhibited above $[BCl_3] = 0.5$ *m* at 170 °C.

The depression of the overall reaction rate at high $[BCl_3]$ has been reported previously by Horn et al.,[14,15] who suggested that BCl_3 could form an acid–base adduct with the nitrogen lone-pair electrons on I and thereby prevent propagation. The ^{31}P NMR data presented[14,15] are one basis for this assertion. Further support for the proposal is the well-documented existence of a variety of BX_3–amine adducts, and the existence of the stable adduct $AlBr_3{:}I$.[16] We can then envision an equilibrium involving BCl_3 and I as part of initiation (eq 7). In this proposal the adduct

$$BCl_3 + (NPCl_2)_3 \overset{K_1}{\rightleftharpoons} \underset{VI}{Cl_3B{:}(NPCl_2)_3} \xrightarrow[\text{initiation}]{} IV \quad (7)$$

VI is inert to propagation and K_1 must be small to account for the very high concentrations of BCl_3 needed to prevent propagation. Other than Horn's observations,[14,15] evidence for the existence of the equilibrium K_1 is the effect of temperature on the reaction at high BCl_3 concentrations. No high polymer was produced at 170 °C and $[I] = 0.27$ *m* when the BCl_3 concentration was greater than ca. 3 *m*. Increasing the temperature induced polymerization. This behavior is expected for an equilibrium system where, if the equilibrium were exothermic then raising the temperature would shift it away from the nonpropagating adduct VI.

Propagation. The propagation reaction was easily studied since rates of propagation were directly measured by Raman spectroscopy at BCl_3 concentrations between 0 and 0.5 *m*. It is clear that this is the case because the products formed at these conditions have molecular weights ranging from 50 000 to 405 000, corresponding to chain lengths of 70–560 units of I. Initiation accounts for less than 1.4% of the total consumption of I. The dramatic rate increases at increasing low $[BCl_3]$ (Figures 2 and 3) suggest that BCl_3 is catalyzing propagation. Propagation is the reaction of the activated chain end with a molecule of I. It is important to note that I is very much in excess of BCl_3 in the region $[BCl_3] = 0$–0.05 *m*. It seems unlikely under these conditions that an interaction between BCl_3 and unreacted I would give rise to this effect. It is reasonable to assume that BCl_3 affects the growing end of the chain, which is in low concentration relative to BCl_3. One possible way for BCl_3 to react with a cationic chain end is via reaction 8, which might be expected to increase the activity of the chain end by providing a counterion that is less tightly bound.

$$\text{-}(NPCl_2)_n\text{-}N{=}PCl_2{}^+Cl^- + BCl_3 \rightleftharpoons \text{-}(NPCl_2)_n\text{-}N{=}PCl_2{}^+BCl_4{}^- \quad (8)$$

At this point a scheme for propagation can be proposed (eq 9) which incorporates reaction 8. In eq 9 an initiation

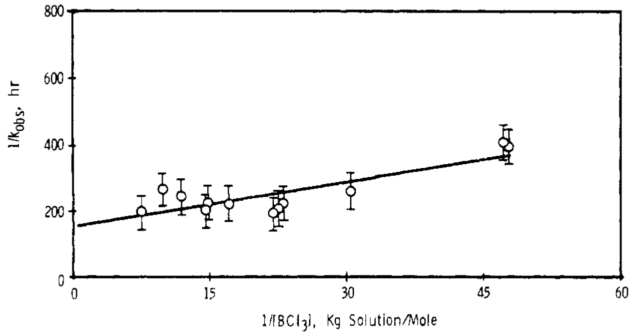
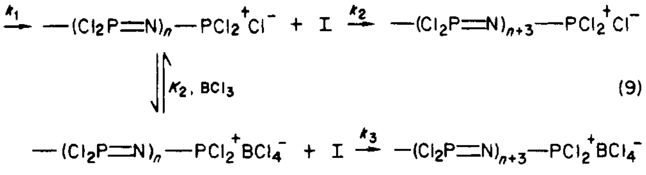


Figure 8. Plot of $1/k_{\mathrm{obsd}}$ vs. $1/[\mathrm{BCl_3}]$ at 170 °C and 0.54 m $[\mathrm{I}]_0$.

Table III
Temperature Dependence of the Rate Constant k_3 and the Equilibrium Constant K_2 for Propagation

temp, °C	k_3, h^{-1}	K_2, (kg of soln)/mol
170	6.56×10^{-3}	33
190	3.69×10^{-2}	5.3
210	1.61×10^{-1}	2.2
230	8.12×10^{-1}	0.68

step with rate constant k_1 generates a fragment with an active chain end. This group can react with I (rate constant k_2) to lengthen the chain. The chain end can also react with $\mathrm{BCl_3}$ with an equilibrium constant K_2 to form a complexed end which is much more reactive toward I than the original chain end. The $\mathrm{BCl_3}$-complexed chain end can then react with I to propagate the chain with rate constant k_3. The existence of a rapid equilibrium is supported by the observation that degassing the system in midreaction causes a sharp rate decrease. Since the plot of k_{obsd} vs. $\mathrm{BCl_3}$ at 170 °C passes through the origin (Figure 2), it is reasonable to assume that k_2 is negligible at 170 °C.



$$\begin{array}{l} \xrightarrow{k_1} -(\mathrm{Cl_2P{=}N})_n-\overset{+}{\mathrm{P}}\mathrm{Cl_2}\,\mathrm{Cl}^- + \mathrm{I} \xrightarrow{k_2} -(\mathrm{Cl_2P{=}N})_{n+3}-\overset{+}{\mathrm{P}}\mathrm{Cl_2}\,\mathrm{Cl}^- \\ \qquad \Big\updownarrow K_2,\ \mathrm{BCl_3} \\ -(\mathrm{Cl_2P{=}N})_n-\overset{+}{\mathrm{P}}\mathrm{Cl_2}\,\mathrm{BCl_4}^- + \mathrm{I} \xrightarrow{k_3} -(\mathrm{Cl_2P{=}N})_{n+3}-\overset{+}{\mathrm{P}}\mathrm{Cl_2}\,\mathrm{BCl_4}^- \end{array} \tag{9}$$

Assuming that the propagation reaction governed by k_3 is the only process significantly contributing to the disappearance of I and that I is always in large excess, the following expression can be written for k_{obsd} at low $[\mathrm{BCl_3}]$.

$$k_{\mathrm{obsd}} = k_3K_2[\mathrm{BCl_3}]/(1 + K_2[\mathrm{BCl_3}]) \tag{10}$$

Inverting eq 10 gives

$$1/k_{\mathrm{obsd}} = 1/k_3 + 1/k_3K_2[\mathrm{BCl_3}] \tag{11}$$

Plotting $1/k_{\mathrm{obsd}}$ vs. $1/[\mathrm{BCl_3}]$ results in the line shown in Figure 8. Thus, $K_2 = 33 \pm 3$ (kg of solution)/mol and $k_3 = (6.6 \pm 0.6) \times 10^{-3}$ h^{-1} at 170 °C. The large value of K_2 is consistent with the sharp increase in k_{obsd} from $[\mathrm{BCl_3}] = 0$ to $[\mathrm{BCl_3}] = 0.05$ m. The saturation of this equilibrium causes the invariance of k_{obsd} above $[\mathrm{BCl_3}] = 0.05$ m. Inserting the values of k_3 and K_2 into eq 10 gives a theoretical plot in excellent agreement with the data (Figure 2).

The effect of temperature on the reaction rate provides additional information about the propagation step. Repeating the calculations just detailed for rate data obtained at 190, 210, and 230 °C gives the parameters shown in Table III. Plots of ln (k_3) vs. $1/T$ are linear, indicating Arrhenius behavior throughout this temperature range. The activation energy of propagation is $\Delta H^{\ddagger}_3 = 36 \pm 4$ kcal/mol, compared with values of 42–57 kcal/mol reported for the uncatalyzed reaction.[17-19] A plot of ln (K_2) vs. $1/T$ is linear, with $\Delta H_2 = -28 \pm 4$ kcal/mol. This exothermic value corresponds to the observed shift of equilibrium K_2 in favor of the reactants as the temperature is raised.

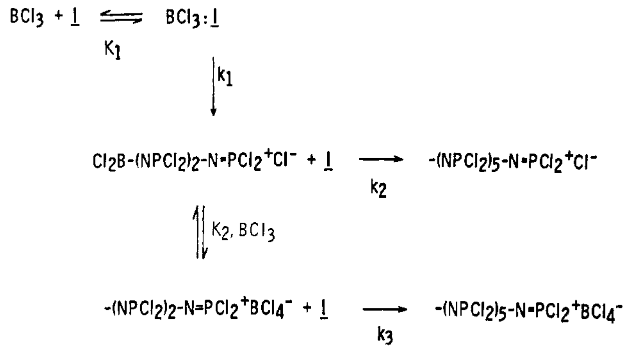


Figure 9. Proposed mechanism for the $\mathrm{BCl_3}$-catalyzed polymerization of I.

The calculated value of ΔS_2 at 170 °C is -56 ± 7 cal/(deg mol). A negative value of ΔS_2 is to be expected for ion pair formation from two neutral molecules. The magnitude of the entropy change is unusual, however, and may indicate some ordering of solvent molecules in conjunction with ion pair formation.

Catalysis Mechanism. Figure 9 illustrates the proposed catalytic mechanism. The dependence of k_{obsd} on $[\mathrm{BCl_3}]$ (Figures 2 and 3) clearly indicates the saturation of an equilibrium. The reversibility of the reaction between $\mathrm{BCl_3}$ and the chain end is demonstrated when the temperature is raised (Table III) or when $\mathrm{BCl_3}$ is removed from a polymerization in midreaction (rate decrease). These effects are observed over a range of temperatures, and in all cases the observed data agree well with calculated values based on the proposed mechanism.

The nature of the interaction between $\mathrm{BCl_3}$ and the growing chain end remains speculative, as no direct evidence exists for the presence of $\mathrm{BCl_4}^-$ in the system. However, the chemistry of $\mathrm{BCl_3}$ and I and particularly the compounds prepared by Moran[13] are consistent with our mechanism.

The activation energy for propagation, $\Delta H^{\ddagger}_3$, leaves little doubt that the effect of $\mathrm{BCl_3}$ on propagation is catalytic, lowering the activation energy by 8–19 kcal/mol (depending on which published value of $\Delta H^{\ddagger}_2$ for the uncatalyzed reaction one chooses to accept).[17-19]

The proposed mechanism for initiation relies more on indirect evidence than that for propagation. While no ring-opened derivative of I has been identified conclusively, neither is there direct evidence for chloride abstraction. An argument in favor of the ring-opening proposal is that one would expect a chloride abstraction process to be fast (consider the ready formation of $\mathrm{BCl_4}^-$ in the reaction of $\mathrm{BCl_3}$ with V at room temperature). However, the initiation step is apparently quite slow. Another consideration is that the presence of the cyclic tetramer $(\mathrm{NPCl_2})_4$ lowers the uncatalyzed polymerization rate even though the P–Cl bond in tetramer is more labile than in I.[3]

The proposed equilibrium in the initiation reaction is necessary to explain the inhibition of propagation by high concentrations of $\mathrm{BCl_3}$ (Figure 4). The reversibility of the effect with increasing temperature supports the proposal of an exothermic equilibrium governed by K_1. The proposed adduct formation is supported both by precedent and by Horn's observations of the ^{31}P NMR spectrum of $\mathrm{BCl_3}$ and derivatives of I. Given the high electron affinity of $\mathrm{BCl_3}$ and the fact that I is the strongest base in the system, the association seems inevitable. $\mathrm{BCl_3}$ should promote ring opening of I by withdrawing electron density from the P–N bonds. It has been shown repeatedly at 170 °C without BCl_3 present that I remains unchanged over long periods of time while polymerization is facile at this temperature when BCl_3 is present.

The absence of a termination step is indicated by the molecular weight dependence on conversion (Table II) and the ability to start and stop the reaction without affecting k_{obsd}.

Conclusions

BCl_3 has both advantages and limitations as a catalyst for the polymerization of I. Optimum rates of propagation require BCl_3 in excess of [II] throughout the course of the reaction. This excess of catalyst imposes a state of continuous initiation on the system and does not give extremely high molecular weight polymers or polymers with narrow molecular weight distributions. In addition, the kinetic activation parameters favor propagation over initiation as the temperature is increased. This defeats one of the primary objectives of using a catalyst, which is to lower the polymerization temperature.

One advantage of the BCl_3-catalyzed system is that high yields of un-cross-linked polymer are produced consistently. The reason for this benefit is not fully understood, but it may be due to steric factors, as follows. The nitrogen atom of the phosphazene molecule is the most probable site of attack of the cationic chain end and it is apparent from models of the polymer chain and I that the N atoms in I are more accessible than those in the polymer.[20,21] The effect of steric hindrance is more likely to be a factor in the catalyzed polymerization since the size of the ion pair at the chain end (BCl_4^-) is much larger than in the uncatalyzed system (Cl^-).

Research in our laboratories is directed at positive identification of the polymer end groups, identification of the initiation products, and further enhancement of the reactivity of the growing chain end.

Registry No. I, 940-71-6; II (SRU), 26085-02-9; II (homopolymer), 25231-98-5; BCl_3, 10294-34-5; triphenyl phosphate, 115-86-6.

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Holographic Relaxation Spectroscopy of Human IgG: Photoinduced Aggregation

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ABSTRACT: Holographic relaxation spectroscopy (HRS) was used to study diffusion and photoinduced reactions of human immunoglobulin G (IgG) labeled with 5-isothiocyanatofluorescein (FITC) and *p*-isothiocyanatoazobenzene (ABITC). Excitation with 488-nm pulses was found to induce aggregation of IgG-FITC, which was initially monomeric. The laser-induced gratings could be detected by diffraction because of the different diffusion rates of the monomers and aggregates. The diffusion coefficients, extrapolated to zero concentration, for the fast and slow species were $(4.5 \pm 0.5) \times 10^{-7}$ and $(2.1 \pm 0.1) \times 10^{-7}$ cm^2/s, respectively. Aggregation was inhibited both by the introduction of reducing agents and by the removal of oxygen, suggesting protein cross-linking assisted by singlet oxygen. IgG-ABITC prepared with pH greater than 11 initially consisted of aggregates, and excitation at 488 nm again produced a grating of monomers and aggregates. However, in this case reducing agents and the removal of oxygen had little effect. Photodisaggregation associated with the trans–cis conformational change of ABITC is suggested.

Introduction

Immunoglobulins are a diverse group of proteins which are synthesized by lymphocytes that form part of the human host defense mechanism. The biological function of the immunoglobulins, or antibodies, involves at least in part the interaction of the immunoglobulin with another species, the antigen. The antigen–antibody reaction may occur in solution or on the surface of a cell. In any event the position and orientation of the antibody with respect to the antigen are critical since the Fab portion of the

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