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Monomer Concentration Effects on the Kinetics and Mechanism of the Boron Trichloride Catalyzed Solution Polymerization of Hexachlorocyclotriphosphazene

Marie Kayser Potts,* Gary L. Hagnauer, and Michael S. Sennett

Polymer Research Branch, Army Materials Technology Laboratory, Watertown, Massachusetts 02172-0001

Geoffrey Davies

Department of Chemistry, Northeastern University, Boston, Massachusetts 02115.

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ABSTRACT: The boron trichloride catalyzed solution polymerization of hexachlorcyclotriphosphazene ($(NPCl_2)_3$) to poly(dichlorophosphazene) ($(NPCl_2)_n$) in 1,2,4-trichlorobenzene solution has been investigated in an attempt to elucidate its reaction mechanism. An earlier proposed mechanism involving initiation, catalysis, and inhibition by BCl_3 has been modified to account for the concentration of trimer in the reaction mixture. Reaction rates were determined by the monitoring of $(NPCl_2)_3$ concentrations with laser Raman spectroscopy and high-performance size-exclusion chromatography and by gravimetric determinations of polymer yields. Polymeric products were characterized by laser light scattering and dilute solution viscometry. Small amounts of polymer chain branching were indicated from the characterization studies.

I. Introduction

The usual method of preparing linear high molecular weight poly(dichlorophosphazene) (II) (the precursor to many poly(organophosphazenes)) is the thermal polymerization of hexachlorocyclotriphosphazene (I) (eq 1),

$$\underset{\mathrm{I}}{(NPCl_2)_3} \xrightarrow{\Delta} \underset{\mathrm{II}}{(NPCl_2)_n} \qquad (1)$$

generally believed to be a cationic chain growth polymerization.[1-3] Due to the high temperature required for uncatalyzed polymerization (ca. 250 °C) and the general irreproducibility of the polymerization with respect to molecular weight and cross-link content,[4,5] a great many materials have been used as catalysts to promote and control the reaction at lower temperatures.[5-7] Boron trichloride (BCl_3) is an effective catalyst for reaction 1 and leads to high yields of soluble polymer at temperatures as low as 150 °C.[8]

A previous kinetic study performed in our laboratory[9] proposed a mechanism for the boron trichloride catalyzed thermal polymerization of I in which BCl_3 acts as a polymerization initiator, catalyst for chain propagation, and a chain growth inhibitor under various conditions. However, the previous study did not examine the effects of the initial concentration of monomer, $[I]_0$, on the rates of polymerization. We have recently studied the effect of monomer concentration in 1,2,4-trichlorobenzene (TCB) solution on the polymerization rates and have modified the original proposal to account for the effects of $[I]_0$.

II. Experimental Section

Materials. Toluene and heptane were distilled from CaH_2 under N_2 and stored under N_2. Spectrophotometric grade TCB (Aldrich) and HPLC grade tetrahydrofuran (Caledon Laboratories, Ltd.) were used as received. Pentane (Caledon Laboratories, Ltd., 98.5%) was saturated with N_2 upon opening and stored under N_2. BCl_3 (C.P. grade, 99.5%) from Matheson Gas Products was used as received. Hexachlorocyclotriphosphazene was obtained from two different sources: 3PNC (99.5% pure) from Shin Nisso Kako Co., Japan, was sublimed under vacuum to remove residual solvent; Phosnic 390 (containing about 5% cyclic tetramer) from Inabata Co., Japan, was repeatedly recrystallized from heptane and sublimed. No differences were noted in the polymerization of I from the different sources.

General Polymerization Procedures. Polymerization reactions (1) were carried out in heavy-walled evacuated sealed glass tubes (25 mm o.d. × 50 mm, tapering to 5 mm o.d. × 70 mm) of approximate volume 25 mL. The smaller end of the polymerization ampule fits into the Raman spectrometer for in situ Raman measurements, while the larger end allowed larger quantities of polymer to be prepared for subsequent characterization.

In the glovebox, a flame-dried ampule was filled with approximately 10 g of a mixture of I and TCB. The tube was degassed outside the glovebox with a vacuum line and ultrasonic agitation. A measured quantity of BCl_3 (0.1–0.4 g) was condensed into the ampule by cooling with liquid nitrogen; the tube was then sealed with a flame. The tubes were subsequently heated at 200 ± 1 °C in a Fisher Iso-temp Model 350 oven.

Poly(dichlorophosphazene) (II) was isolated from the reaction tubes in the glovebox by precipitation with pentane, redissolving the precipitate in a minimum amount of toluene and precipitating again with more pentane.

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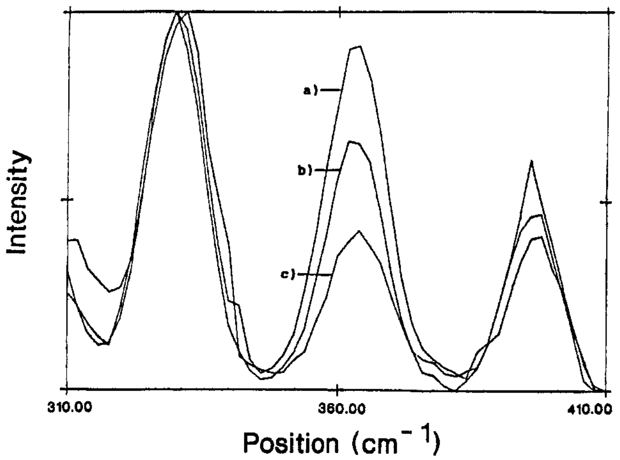

Figure 1. In situ Raman spectra recorded during polymerization of I for $[I]_0 = 0.96$ *m* and $[BCl_3]_0 = 0.096$ *m*. Polymerization times are (a) 0, (b) 10, and (c) 17 h.

Table I
HPSEC Conditions

sample concentn, % (w/v)	0.05–0.3
injection vol, μL	10–20
mobile phase	THF with helium sparge
flow rate, mL/min	1
columns	IBM 5 μM particle size, low molecular weight set ($M < 2 \times 10^4$)
detection	refractive index
analysis time, min	29

Instrumentation. Raman measurements were made with a Spex Industries Ramalog 1401 double spectrometer coupled to a Datamate DM1 controller. The light source was a Spectra Physics Model 164 2-W argon ion laser operating at a wavelength of 488 nm with 800 mW of incident power. For reaction rates monitored by Raman spectroscopy, an initial Raman spectrum (time = 0 h) was recorded at room temperature from 310 to 410 cm^{-1}. The reaction tubes were heated for a period of time and cooled to room temperature, and the Raman spectrum was recorded again. The decrease in intensity of the peak due to the PCl_2 symmetric stretch[10] in I (364 cm^{-1}) was proportional to the amount of I that had reacted. The peak intensity at 327 or 390 cm^{-1} (1,2,4-trichlorobenzene) was used as an internal reference. The Raman spectra recorded as a function of time for a particular reaction are illustrated in Figure 1.

High-performance size-exclusion chromatography (HPSEC) was also used to monitor reaction rates. A calibration curve was constructed from the areas of the elution peaks of several standard TCB solutions of I, which was used to determine unknown concentrations of I isolated from reaction ampules. The HPSEC system was comprised of a Waters M6000A solvent delivery system, U6K injector, 410 differential refractometer detector, and a low molecular weight column set in a Jordi column oven (35 °C). A Waters Model 840 data system was used to collect and process data. The detailed chromatographic conditions are listed in Table I.

Total integrated intensity light-scattering measurements were performed on a Brookhaven Instruments BI-200SM goniometer and BI-2030 correlator. The light source was the 633-nm line of a Melles Griot 5-mW helium–neon laser. Due to the hydrolytic instability of II, care was taken to exclude moisture from the polymer solutions. Toluene solutions of II were prepared in the glovebox and filtered (0.2 μM PTFE membrane filters) outside the glovebox directly into the light-scattering cells, which were capped with ground-glass joints. The refractive index increment of II in toluene[11] and the Rayleigh ratio of the calibration liquid (toluene)[12] were 0.06 mL/g and 1.40×10^{-5} cm^{-1}, respectively.

Dilute-solution viscosity measurements of TCB solutions were made with Cannon Ubbelohde viscometers immersed in a 40 L water bath maintained at 41.0 ± 0.1 °C. Single-point intrinsic viscosities were determined by diluting a small quantity of the polymerized solutions (containing unreacted I) with TCB and measuring the resulting flow times; in each case the concentration of II had been determined from the kinetic studies.

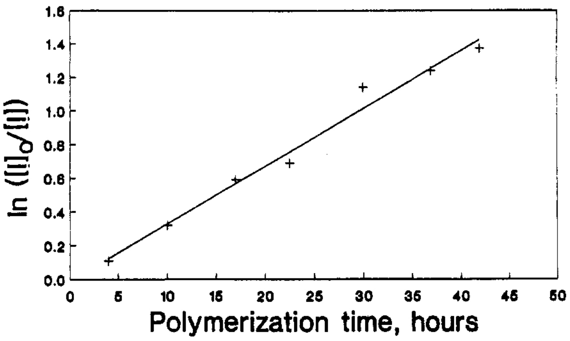

Figure 2. Decrease in [I] as a function of polymerization time for $[I]_0 = 0.96$ *m* and $[BCl_3]_0 = 0.096$ *m*, showing first-order reaction kinetics.

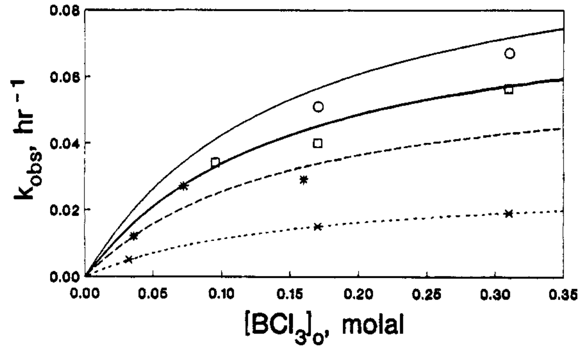

Figure 3. Dependence of k_{obs} on $[BCl_3]_0$ for various $[I]_0$: (×) 0.32, (*) 0.72, [□] 0.96, and (○) 1.2 *m*. Lines were fit to eq 3 for the various $[I]_0$: (···) $[I]_0 = 0.32$ *m*, (- - -) $[I]_0 = 0.72$ *m*, (—) $[I]_0 = 0.96$ *m*, (—) $[I]_0 = 1.2$ *m*.

III. Results and Discussion

Kinetics and Mechanism. Plots of log $([I]/[I]_0)$ vs polymerization time, where $[I]_0$ and [I] denote initial and instantaneous concentrations of I, were linear for all concentrations of $[I]_0$ in TCB solution used in this study: 0.32, 0.72, 0.96, and 1.2 *m* (10%, 20%, 25%, and 30% by weight, respectively). This indicates an apparent first-order dependence of the polymerization rate on [I] (Figure 2), the same behavior as found in our earlier study.[9]

The observed first-order rate constants, k_{obs}, for various initial concentrations of I are plotted as a function of $[BCl_3]$ in Figure 3. For a particular initial concentration of I, k_{obs} increases sharply with increasing concentrations of boron trichloride and then levels off at a particular concentration of BCl_3. This limiting k_{obs} increases as the concentration of I increases. Thus, the observed rate of reaction depends not only on the concentration of boron trichloride (as observed by Sennett et al.[9]) but also on the initial concentration of I, $[I]_0$.

The rate constants determined at BCl_3 concentrations of 0.17 and 0.31 *m* are plotted as a function of $[I]_0$ in Figure 4. The linear plots show that k_{obs} is directly proportional to the initial concentration of I, demonstrating a pseudo-first-order dependence on $[I]_0$, in which the apparent first-order rate constant depends on the initial concentration of boron trichloride. This dependence on I was not observed previously because the initial concentration of I was not varied.[9]

The previous work by Sennett et al.[9] on the boron trichloride catalyzed polymerization of I led to a proposal for the polymerization mechanism (Figure 5). Boron trichloride was proposed to form a nonpolymerizing adduct with the nitrogen lone-pair electrons of I. At large con-

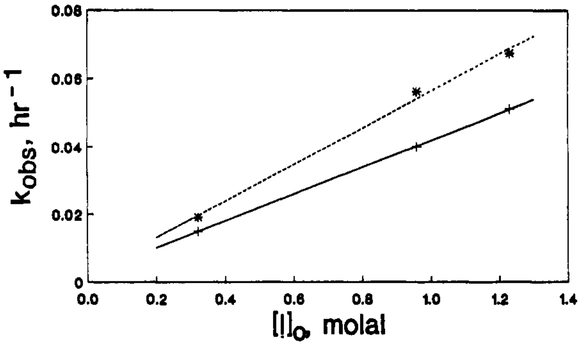

Figure 4. Dependence of k_{obs} on $[I]_0$ for (+) $[BCl_3]_0 = 0.17$ m and (*) $[BCl_3]_0 = 0.31$ m.

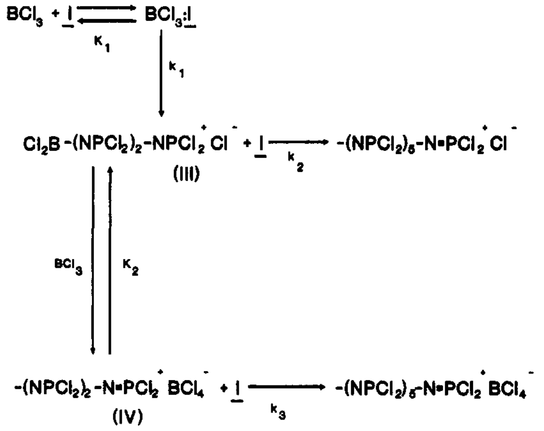

Figure 5. Mechanism proposed by Sennett et al.[9] for the BCl_3-catalyzed thermal polymerization of I.

centrations of BCl_3, most of the I is present as the adduct and little is available to propagate the polymer chain. This explains why the reaction rates become invariant with increasing concentration of BCl_3 at high $[BCl_3]_0$ (Figure 3). The initiation step of the polymerization is believed to be ring opening of the BCl_3–I adduct, although the possibility of abstraction of a chloride ion from the ring has not been ruled out.[13] Either initiation step generates a chloride ion, which can react with other uncomplexed I molecules to lengthen the chain (rate constant k_2) or it can react with free BCl_3 (equilibrium constant K_2) to form a more reactive chain end. The BCl_3-complexed chain end reacts with I with a rate constant k_3, which is much larger than k_2. On the basis of this proposed mechanism, Sennett et al.[9] derived an expression for the dependence of the observed rate constant on the concentration of boron trichloride. This rate constant appeared to be first-order, since the dependence of the reaction on $[I]_0$ was not known.

The data shown in Figures 3 and 4 support the proposed mechanism (Figure 5) and rate law with a slight modification necessary to account for the linear dependence of the observed reaction rate on the initial concentration of trimer. This modified rate law may be expressed as shown in eq 2.

$$k_{obs} = \frac{k_3K_2[BCl_3]_0}{1 + K_2[BCl_3]_0}[I]_0 \qquad (2)$$

Inverting eq 2 yields eq 3, from which the values of k_3 and K_2 can be determined graphically. For each value of $[I]_0$, the reciprocal of k_{obs} plotted against the reciprocal of the initial boron trichloride concentration yields the rate and equilibrium constants from the y intercept and the slope, respectively (Figure 6).

$$\frac{1}{k_{obs}} = \frac{1}{k_3[I]_0} + \frac{1}{k_3K_2[I]_0[BCl_3]_0} \qquad (3)$$

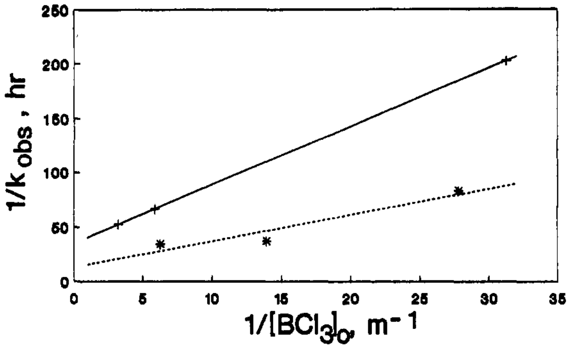

Figure 6. Dependence of $1/k_{obs}$ on $1/[BCl_3]_0$ for (+) $[I]_0 = 0.32$ m and (*) $[I]_0 = 0.72$ m.

Table II
Calculated and Experimental Values of k_{obs} Dependence on $[I]_0$

$[BCl_3]_0$, m	calc, h^{-1} m^{-1}	obs, h^{-1} m^{-1}
0.17	0.047	0.040
0.31	0.060	0.054

Table III
Dilute Solution Properties of II

$[\eta]$,[a] dL g^{-1}	10^{-5} M_w, g mol^{-1}	$\langle S^2\rangle_z^{1/2}$, nm	$10^4\langle S^2\rangle_z/M_w$, nm^2 mol g^{-1}	$[I]_0$, m	$[BCl_3]_0$, m	% conv
0.18	1.83	b		0.72	0.072	38
0.22	2.70	b		0.72	0.072	66
0.23	3.73	b		0.72	0.072	73
0.26	4.62	32	22	1.20	0.170	75
0.41	6.18	34	19	0.96	0.096	76
0.38	8.15	38	18	0.96	0.096	80
0.43	9.16	41	19	0.96	0.096	84

[a] 1,2,4-Trichlorobenzene solution, 41 °C. [b] $R_g < {}^1/_{20}$ incident wavelength cannot be determined accurately.

The average values of k_3 and K_2 calculated from the plots of $1/k_{obs}$ vs $1/[BCl_3]_0$ are 0.089 ± 0.013 h^{-1} m^{-1} and 6.6 ± 1.5 m^{-1}, respectively. The fact that these plots are linear validates the proposed mechanism. Curves fit to eq 2 with the average values of k_3 and K_2 and the appropriate experimental values of $[BCl_3]_0$ and $[I]_0$ are included with the experimental rate data in Figure 3. Agreement between the experimental data and the curves calculated from eq 2 is good. This further supports our conclusion that the BCl_3 dependence of k_{obs} in the proposed mechanism is correct. An additional test of this mechanism was made by comparing the values of the slopes calculated from Figure 4 to the values of $k_3K_2[BCl_3]_0/(1 + k_2[BCl_3]_0)$ calculated from eq 2, using the experimentally determined values of k_2 and K_3. This comparison is shown in Table II.

Polymer Characterization. Light-scattering measurements were made on a number of poly(dichlorophosphazene) samples isolated from polymerization ampules to determine weight-average molecular weights (M_w), z-average radii of gyration ($\langle S^2\rangle_z^{1/2}$), and second virial coefficients (A_2) in toluene solution. These values, together with single-point intrinsic viscosities in TCB solution, are listed in Table III for the various polymerization conditions.

For a particular set of reaction conditions, M_w was observed to increase as a function of increasing conversion of I to II, as shown in Table III. This behavior is typical of a chain growth polymerization with no termination step (living polymerization). In this type of reaction, the molecular weight of the polymer increases continuously until the supply of monomer is depleted. The absence of a termination step was also noted by Sennett et al.[9]

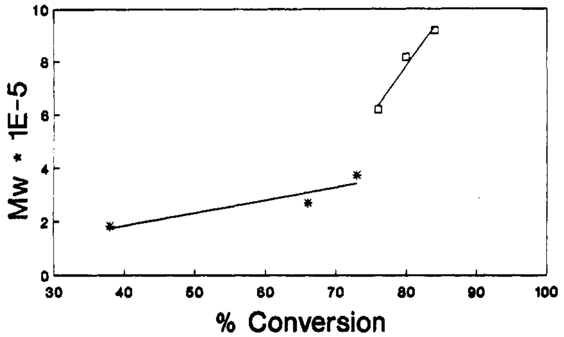

Figure 7. Dependence of the weight-average molecular weight on percent conversion of I for (*) $[I]_0 = 0.72$ *m* and $[BCl_3]_0 = 0.072$ *m* and for (□) $[I]_0 = 0.96$ *m* and $[BCl_3]_0 = 0.096$ *m*.

The average ratio $\langle S^2 \rangle_z / M_w$ (ca. 0.0019 nm^2 mol g^{-1}) determined in this study is smaller than what is typically observed for random-coil polymers in a thermodynamically good solvent (0.003–0.008) and smaller than what was determined earlier by Hagnauer[3,11] for the same polymer–solvent system (0.0033 nm^2 mol g^{-1}), where the polymers were prepared by bulk polymerization at 250 °C with no added catalyst. Values of A_2 (≈ 0) in the present study and in Hagnauer's earlier studies[3,11] suggest that toluene at 25 °C is essentially a Θ solvent for poly(dichlorophosphazene). The square of the radius of gyration divided by the molecular weight $\langle S^2 \rangle_z / M_w$ should be constant for a homologous series of linear randomly coiled polymers in a Θ solvent. Under these conditions, the polymer chain dimensions are at their minimum value.[14] However, values of $\langle S^2 \rangle_z / M_w$ smaller than the minimum value may be obtained when the polymer molecules contain branches, since a branched polymer of the same molecular weight will be more compact and therefore assume a smaller size in solution.

Figure 7 shows a plot of molecular weight vs percent conversion of the first three and last three entries in Table III. The lower molecular weight data set represents polymerizations with $[I]_0 = 0.72$ *m* (20% by weight) and $[BCl_3]_0 = 0.072$ *m*, and the higher molecular weight data set is for polymerizations run at $[I]_0 = 0.96$ *m* (25% by weight) and $[BCl_3]_0 = 0.096$ *m*. The change in slope for the two different polymerization conditions is quite dramatic (increase by a factor of 10), but the observed rate of reaction (for disappearance of [I] is not significantly different (0.027 and 0.034 h^{-1}). The only explanation for a sharp increase in molecular weight without a corresponding increse in the consumption of I during polymerization is the formation of polymer chain branches.

There are two mechanisms of branch formation, which are consistent with the proposed polymerization mechanism (Figure 5). The first mechanism involves attack of a growing chain end (IV in Figure 5) on a nitrogen of another polymer backbone. If this reaction were kinetically favored, a highly branched network would form easily, since the attacking polymer chain can attack a polymer chain that may already contain branches. All polymer II isolated for characterization in this study was soluble in toluene even at high conversions; thus if this mechanism is responsible for chain branching, it does not occur to any significant degree. The earlier work by Sennett et al.[9] on the BCl_3-catalyzed polymerization also produced high molecular weight gel-free polymer at high conversions.

The second reaction scheme which could result in branching involves an equilibrium between a growing chain end (III or IV in Figure 5) and BCl_3. If BCl_3 extracted a chlorine atom from a phosphorous along the polymer chain backbone and formed a cationic chain growth center at that phosphorous, a branch point could propagate by attacking nearby molecules of I (Figure 8). This mechanism is less likely to lead to large amounts of branching and subsequent cross-linking, because the branch would still grow by sequentially adding individual I molecules, as in a normal chain growth polymerization, instead of adding large polymer segments. Since the cation at the end of a polymer chain is probably more reactive than a cation along the polymer backbone for steric reasons, one would expect propagation and thereby branching to occur at points along the polymer chain backbone only when the concentration of I is relatively high as in the present study (0.72–1.2 *m*, compared to 0.54 molal in the work of Sennett et al.[9]).

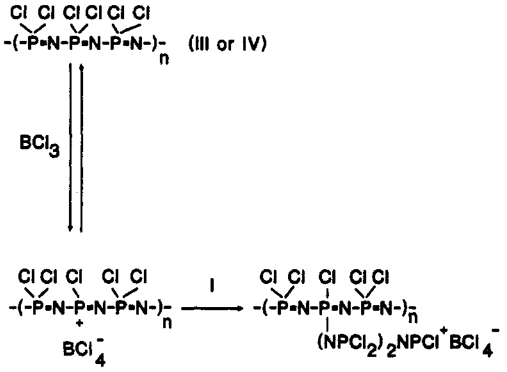

Figure 8. Mechanism proposed for branch formation in the BCl_3-catalyzed thermal polymerization of I at high $[I]_0$.

From the radius of gyration values and the sharp increase in molecular weight with increasing conversion, polymer chain branching seems very likely, but it is not clear from the experimental evidence at this point which mechanism of chain branching is operative.

In general, branching in polymer chains is of two types: long-chain branching, where the length of the branch is comparable to the length of the chain; and short-chain branching, where the length of the chain branches is much smaller than the length of the main chain. Short-chain branching does not affect the radius of gyration significantly and thus generally cannot be detected from light-scattering measurements. Long-chain branching is the most likely type of branching to occur under either of the possible branching mechanisms. The first mechanism involves the attack of a growing chain end on another polymer molecule. This assumes that there is only one active site per growing polymer chain and therefore that there would probably be long but relatively few branch points per chain. In the second mechanism proposal there may be many cationic growth sites along the polymer chain, but the chance for any of these sites to propagate is low. Once one molecule of I has been added at a branch point, however, the propagation rate at that new site would be essentially equivalent to any other chain end.

The extent of branching may be estimated via the following equation[15]

$$\langle g \rangle_z = \frac{\langle S^2 \rangle_{z,b}}{\langle S^2 \rangle_{z,l}} = \frac{1}{1 + B_w/3} \tag{4}$$

for long-chain trifunctional (three polymer segments at a single junction) branching, where the subscripts b and l denote branched and linear chain dimensions, respectively, and B_w is the weight-average number of branch units per polymer chain. Using the values of 0.0019 and 0.0033 for the branched and linear ratios $\langle S^2 \rangle_z / M_w$, B_w is calculated to be 2.2 weight-average branch units per chain. Considering an average M_w of 1.0×10^6 (containing approximately

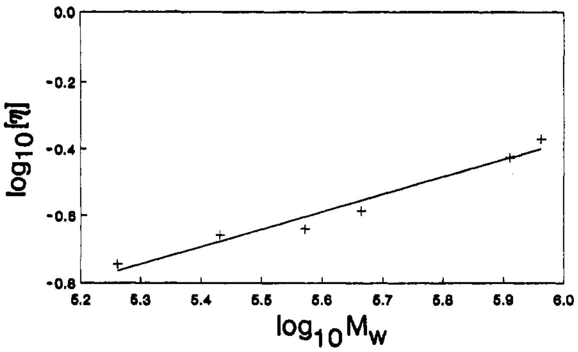

Figure 9. Dependence of log [η] (in TCB solution) on log M_w of II.

8600 weight-average repeat units), a branch point would occur every 3900 repeat units.

Figure 9 shows the log M_w vs log [η], where [η] is the intrinsic viscosity at 41 °C. A Mark–Houwink expression (eq 5) for II in TCB solution covering nearly a decade of molecular weights was determined from the slope and intercept of this plot.

$$[\eta] = 2.9 \times 10^{-4} M_w^{0.53} \qquad (5)$$

The value of the exponent in the Mark–Houwink relationship generally ranges from 0.5 (Θ solvent) to 0.8 (good solvent) for linear randomly coiled polymers. In this case, the exponent is only slightly higher than the expected value for polymer in a Θ solvent. Since TCB is probably not a Θ solvent for II and in fact is probably a relatively good solvent,[16] this small value of the exponent may be due to the effects of branching. The intrinsic viscosity is related to the hydrodynamic volume, which, like the radius of gyration, is smaller for a branched polymer than a linear polymer of the same molecular weight.[14]

IV. Conclusions

The mechanism previously proposed by Sennett et al.[9] for the boron trichloride-catalyzed thermal polymerization of hexachlorocyclotriphosphazene has been shown to be valid over a wide range of initial monomer concentrations. In addition, the previously unknown dependence on the concentration of $[I]_0$ has been demonstrated. We have shown that the molecular weight of un-cross-linked poly(dichlorophosphazene) produced can be controlled by appropriate choice of $[I]_0$ and $[BCl_3]_0$. In general, polymerizations with high initial concentrations of I and which are run to high extents of conversion produce the highest molecular weight polymer. However, there is evidence of a small amount of long-chain polymer branching (which apparently does not lead to cross-linking) under these experimental conditions.

A Mark–Houwink expression relating the intrinsic viscosity of poly(dichlorophosphazene) in 1,2,4-trichlorobenzene solution to the weight-average molecular weight has been determined for molecular weights between 1.8×10^5 and 9.6×10^5.

Current polyphosphazene research in our laboratory is directed toward identification of polymer chain end groups and clarification of the branching mechanism.

Registry No. I, 940-71-6; BCl_3, 10294-34-5.

Supplementary Material Available: Appendix containing the derivation of eq 2 (2 pages). Ordering information is given on any current masthead page.

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