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QUARTERLY PROGRESS REPORT 3

COVERING THE PERIOD

1 DECEMBER 1963 TO 28 FEBRUARY 1964

A NEW TYPE OF POLYMERIZATION INVOLVING ORGANOPHOSPHORUS COMPOUNDS AS CATALYSTS

Prepared by

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ABSTRACT

This program is concerned with determining the feasibility of using a newly found polymerization of N-vinylcarbazole by phosphorus compounds in detecting the presence of toxic air contaminants.

A kinetic study of the polymerization of N-vinylcarbazole at 25°C in methylene chloride with diethylphosphoric acid and diethylchlorophosphate was begun. The results indicate that the hydrolysis of diethylchlorophosphate is very rapid, does not influence the rate of polymerization, and is essentially complete to yield two catalytically active acids. Neither catalyst or water are consumed in the polymerization. The dependence of the rate of the polymerization, at low conversions, on monomer $[M]$, acid $[A]$ and water $[H_2O]$ concentrations is given by $-d[M]/dt = K_o \frac{[A][M]^2}{[H_2O]}$ where $K_{o(verall)}$ is the overall rate constant for the initiation, propagation and termination processes.

The relative catalytic effectiveness of various acids in acetonitrile corresponds qualitatively with their relative acidity in acetonitrile, as indicated by potentiometric measurements on equimolar solutions of these acids.

The sensitivity of the system was determined; 0.04 micrograms of diethylchlorophosphate produces a visually detectable turbidity due to polymerization of N-vinylcarbazole in acetonitrile

within 14 mins. This result was reproducible. Indications are that both time and sensitivity factors can be further improved.

A search for less volatile polar solvent media for the polymerization of N-vinylcarbazole was begun. Polymerization with diethylchlorophosphate occurred in glutaronitrile but not in dimethylsulfoxide.

A stored solution of N-vinylcarbazole in acetonitrile containing 5000 ppm water remained clear and stable for two weeks. This is being reinvestigated because it was later found that the acetonitrile used in this experiment might have contained a trace of an acidic impurity which may have caused premature destabilization.

INTRODUCTION

The general objective of the overall program of which this contract is a part is to develop sensitive practical means of detecting toxic air contaminants. The specific objective of this contract is to determine the feasibility of detecting minute concentrations of contaminants by a chemical amplification method in which contaminants catalyze a readily detectable polymerization of a monomer such as N-vinylcarbazole.

In beginning a kinetic study of the polymerization, dry methylene chloride is being used as the solvent since the polymer precipitates and forms too rapidly in acetonitrile which was used in most previous experiments.

The results are compared with those reported in a series of papers by Brown and Mathieson for the polymerization of styrene catalyzed by chloroacetic acids[1]. We have not found other reports dealing with a detailed kinetic study of a Bronsted-acid-catalyzed vinyl polymerization involving the presence of small amounts of water.

[1] C. P. Brown and A. R. Mathieson, J. Chem. Soc., 1957, 3608-3639 (a series of 5 papers).

RESULTS AND DISCUSSION

Time-conversion plots for two polymerizations in methylene chloride with similar concentrations of diethylphosphoric acid and water and slightly varying monomer concentrations are shown in Figures 1 and 2. Similar plots for a polymerization in which the water content was increased threefold and one in which diethylchlorophosphate (including an equimolar amount of water) was used instead of diethylphosphoric acid are shown in Figures 3 and 4 respectively. The conversions were determined gravimetrically by periodic removal of aliquots from a stirred solution of N-vinylcarbazole in methylene chloride following addition of undiluted catalyst with a hypodermic syringe. The polymerizations were performed under a nitrogen atmosphere. As shown in the corresponding Figures 1A, 2A, 3A and 4A, straight lines are obtained when the reciprocal of the monomer concentration is plotted against time at low conversion, indicating that the rate of polymerization is proportional to the square of the monomer concentration and that the other active components, catalyst and water, are not consumed in the course of the polymerization. The rate of polymerization, however, is dependent on the initial concentrations of water and catalyst as indicated by a further examination of these curves.

During the early stages of polymerization, the rate of the polymerization shown in Figure 2 is about three times as fast as that of the polymerization shown in Figure 3 in which the water

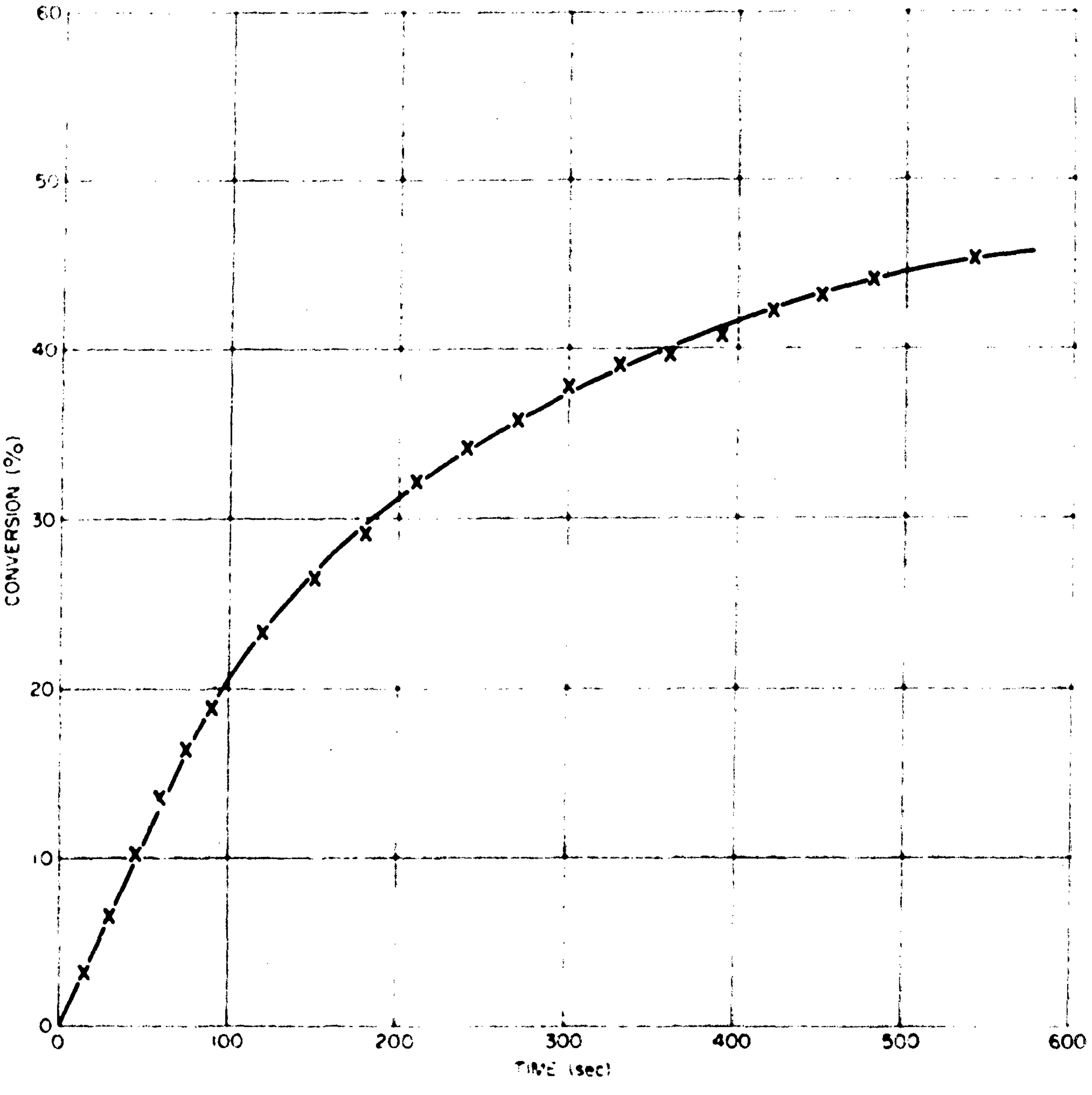

Fig. 1. Time versus Conversion for Polymerization of 0.351 M N-Vinylcarbazole with 0.149 M Diethylphosphoric Acid and 1.75 x 10^{-3} M Water in Methylene Chloride at 25°C.

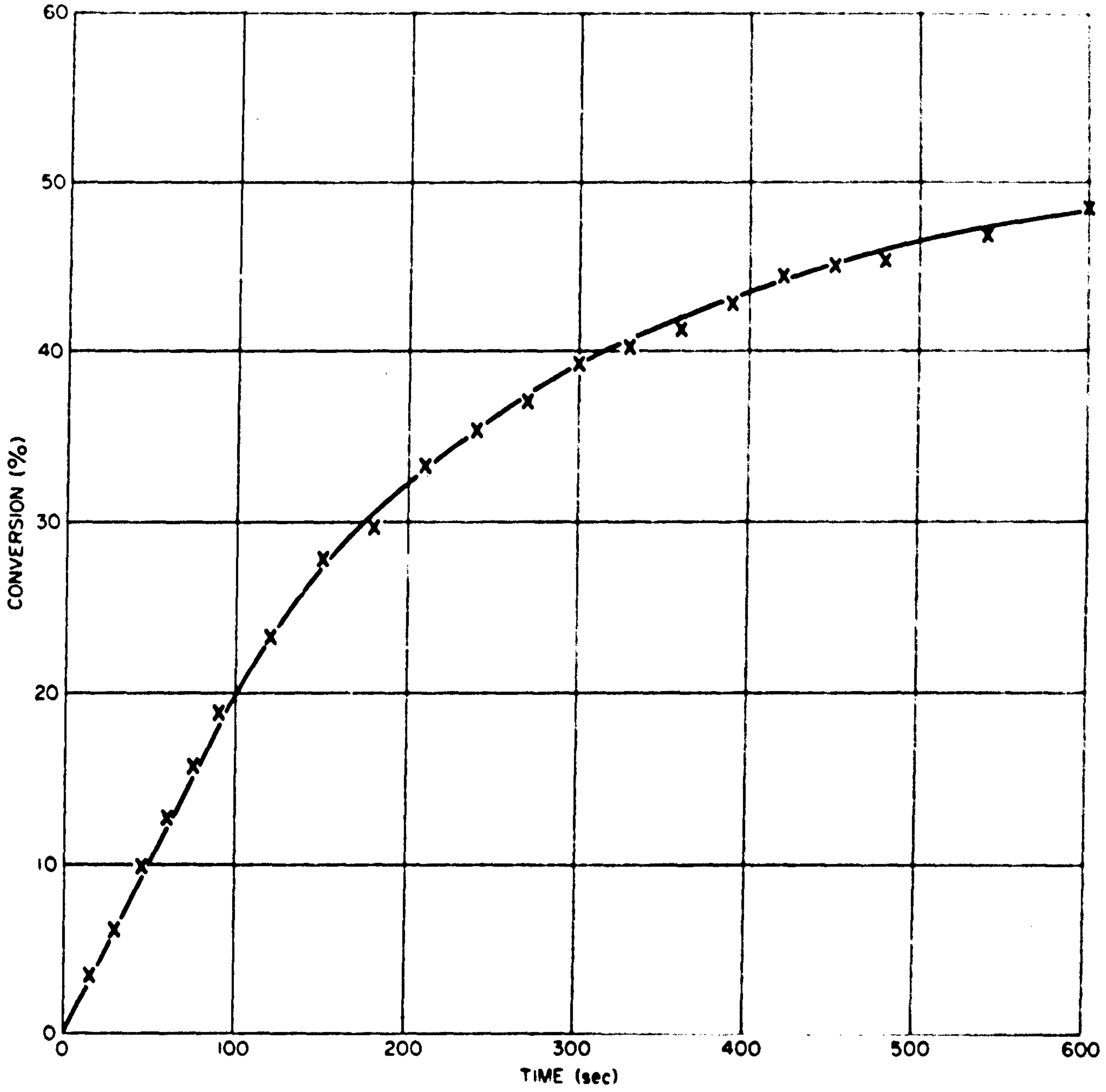

Fig. 2. Time versus Conversion for Polymerization of 0.394 M N-Vinylcarbazole with 0.149 M Diethylphosphoric Acid and 1.78 x 10^{-3} M Water in Methylene Chloride at 25°C.

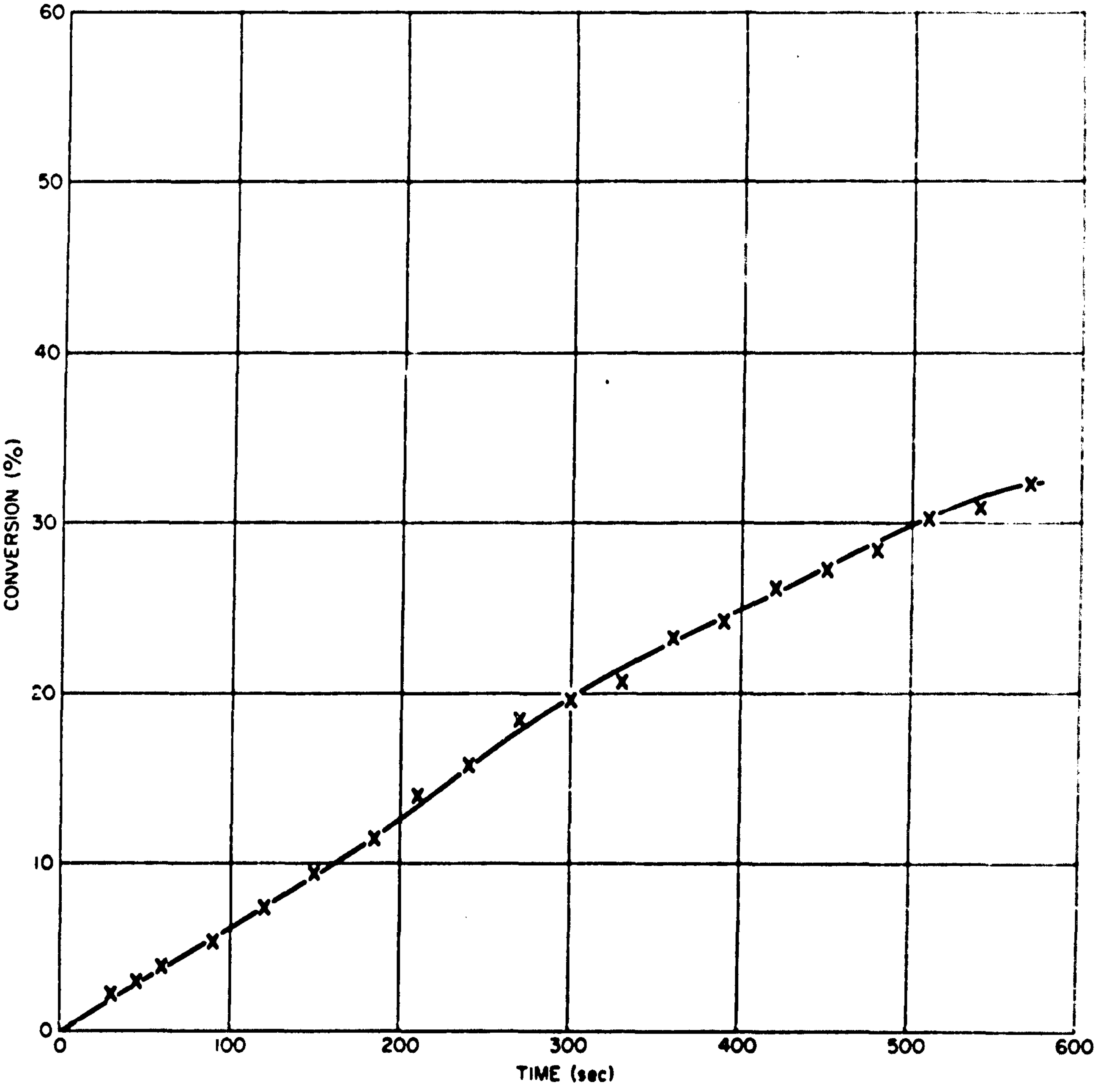

Fig. 3. Time versus Conversion for Polymerization of 0.419 M N-Vinylcarbazole with 0.149 M Diethylphosphoric Acid and 5.5^{6} x 10^{-3} M Water in Methylene Chloride at 25°C.

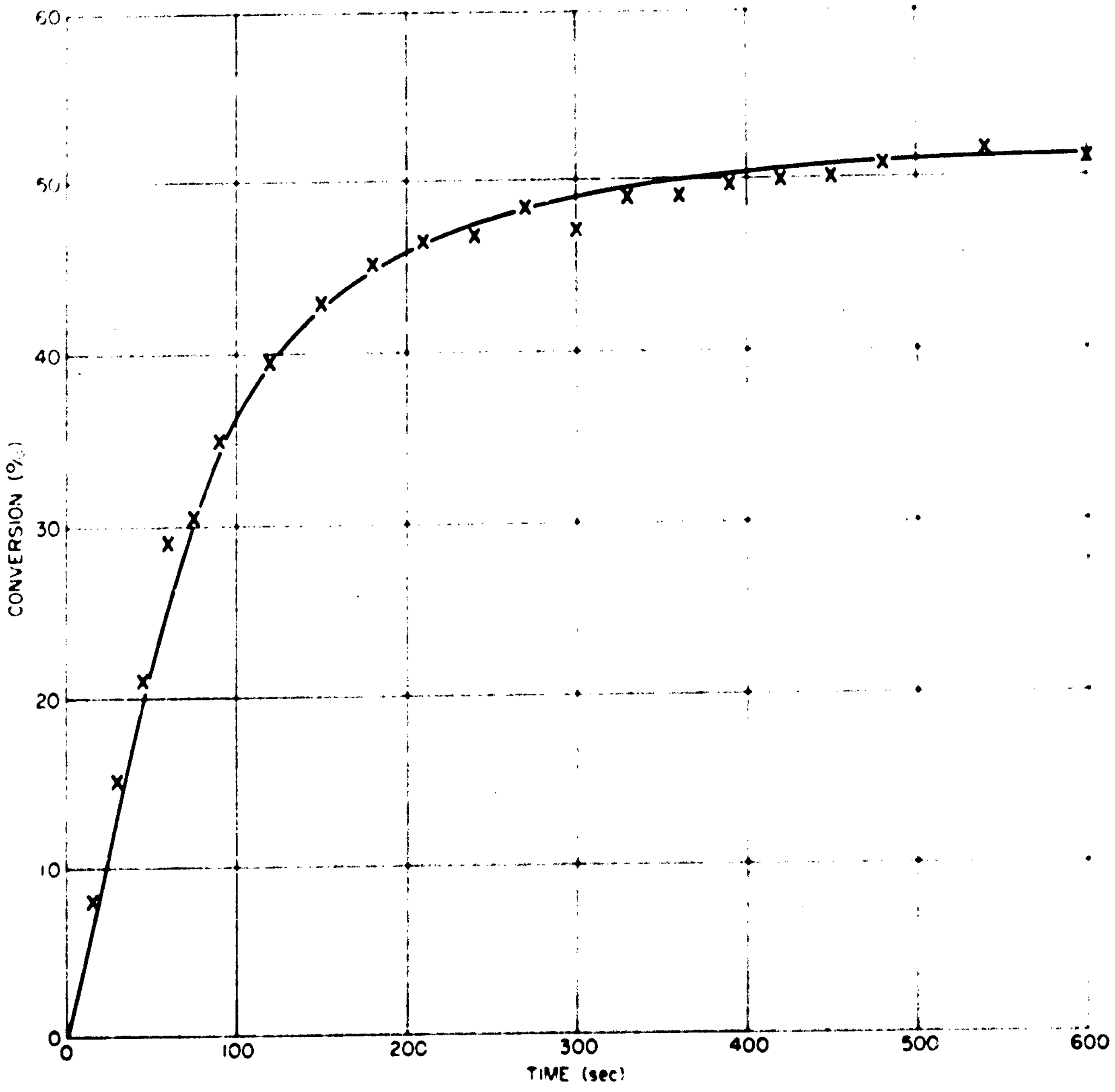

Fig. 4 Time versus Conversion for Polymerization of [illegible].2[illegible] M N-Vinylcarbazole with [illegible] M Diethylchlorophosphate and [illegible].14[illegible] M Water (1.[illegible] x $10^{-[illegible]}$ M water is the theoretical concentration retarding polymerization after hydrolysis of diethylchlorophosphate: see last paragraph on p. 15).

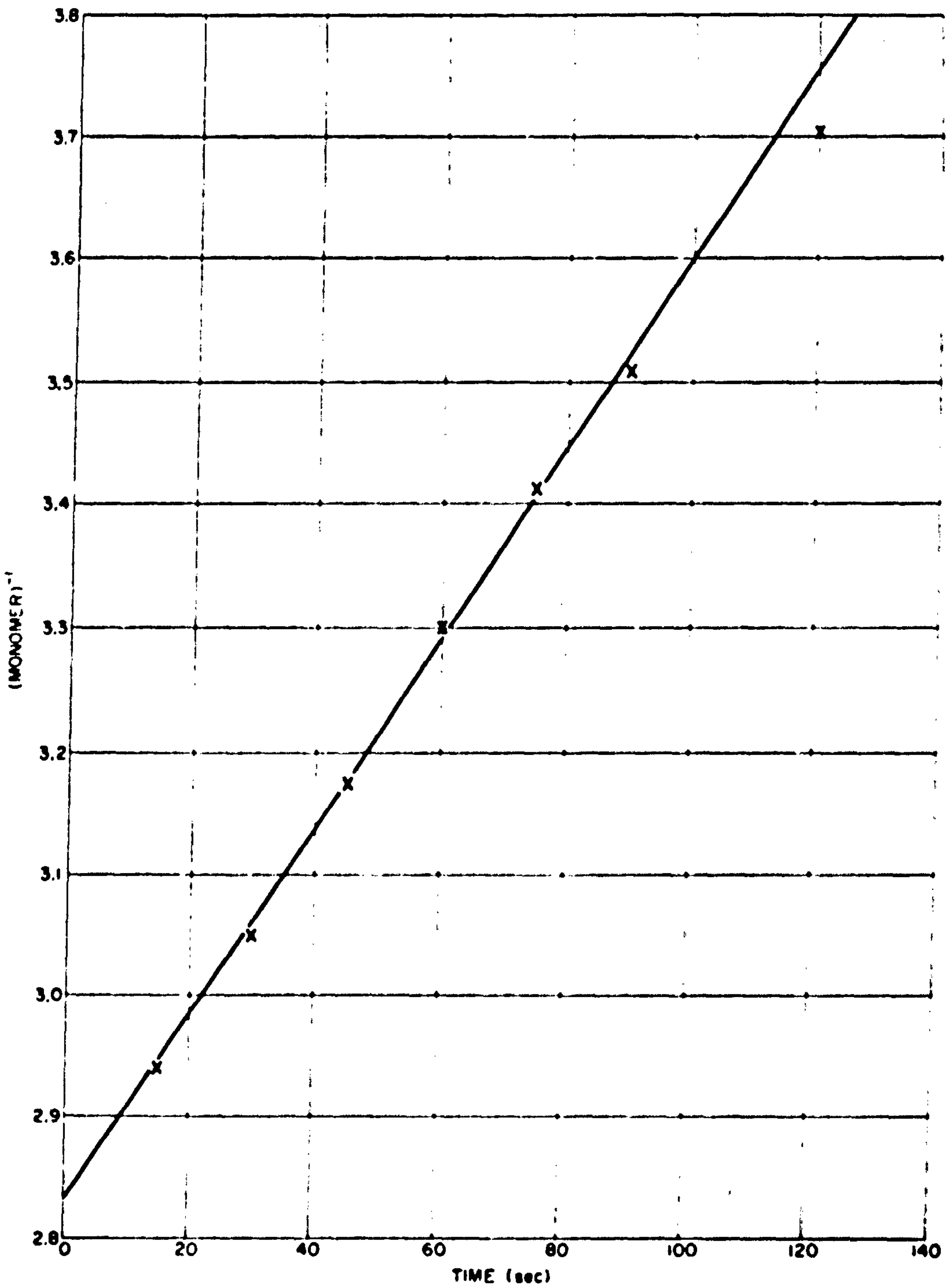

Fig. 1A. Time versus Reciprocal of Monomer Concentration in Polymerization of 0.351 M N-Vinylcarbazole with 0.149 M Diethylphosphoric Acid and 1.78 x 10^{-3} M Water in Methylene Chloride at 25°C.

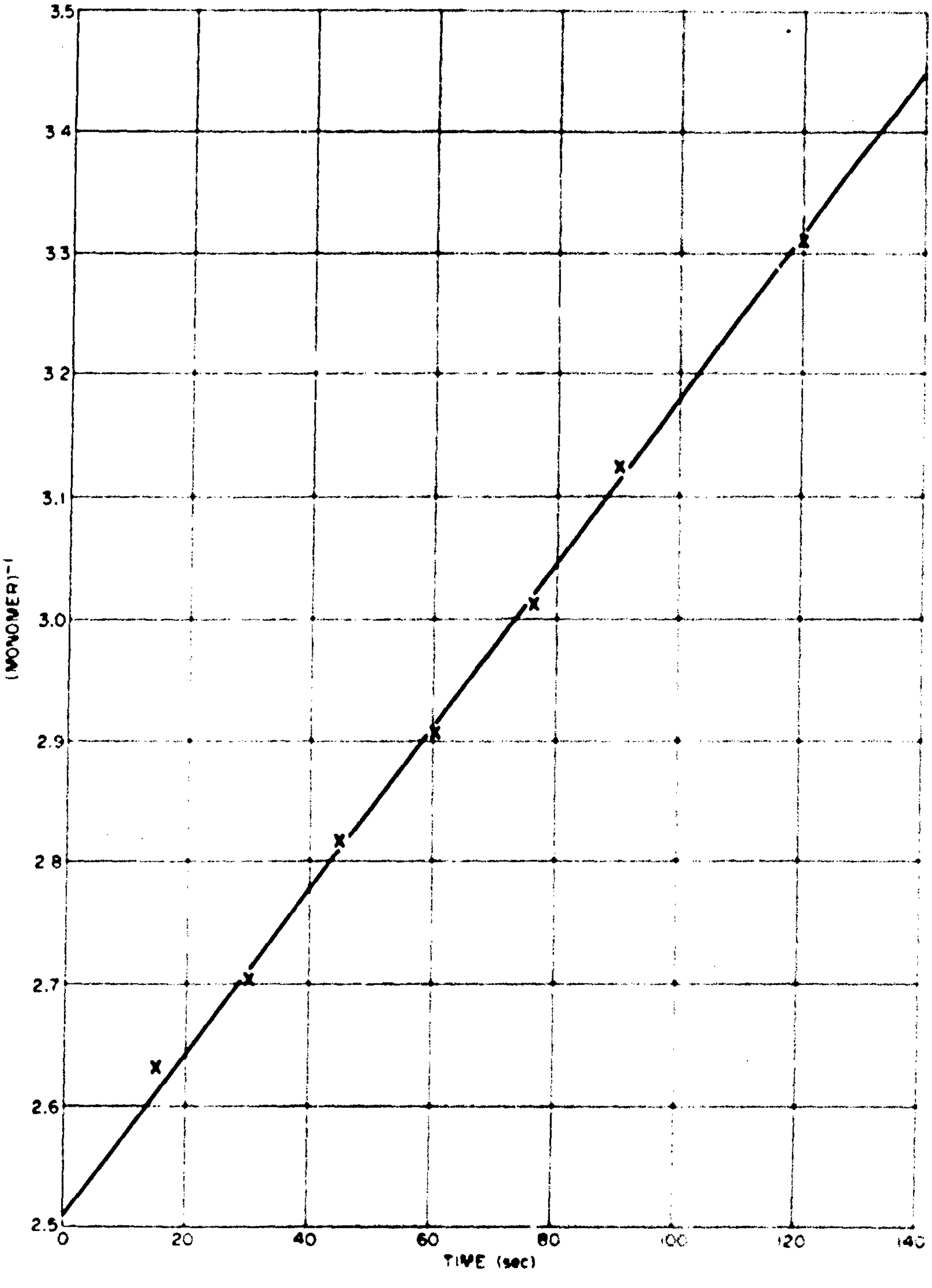

Fig. 2A. Time versus Reciprocal of Monomer Concentration in Polymerization of 0.398 M N-Vinylcarbazole with 0.149 M Diethylphosphoric Acid and 1.78 x 10^{-3} M Water in Methylene Chloride at 25°C.

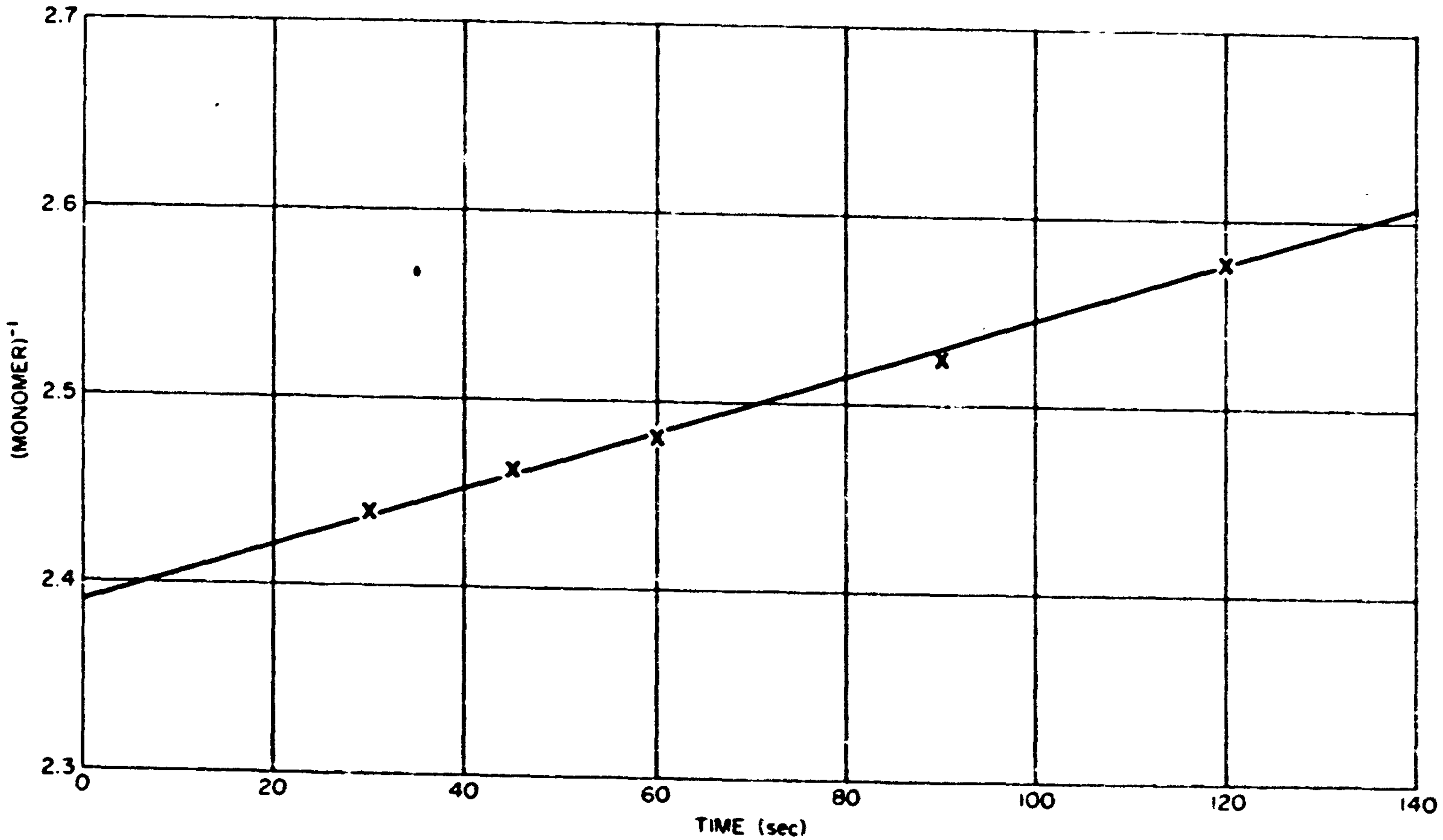

Fig. 3A. Time versus Reciprocal of Monomer Concentration in Polymerization of 0.419 M N-Vinylcarbazole with 0.149 M Diethylphosphoric Acid and 5.56×10^{-3} M Water in Methylene Chloride at 25°C.

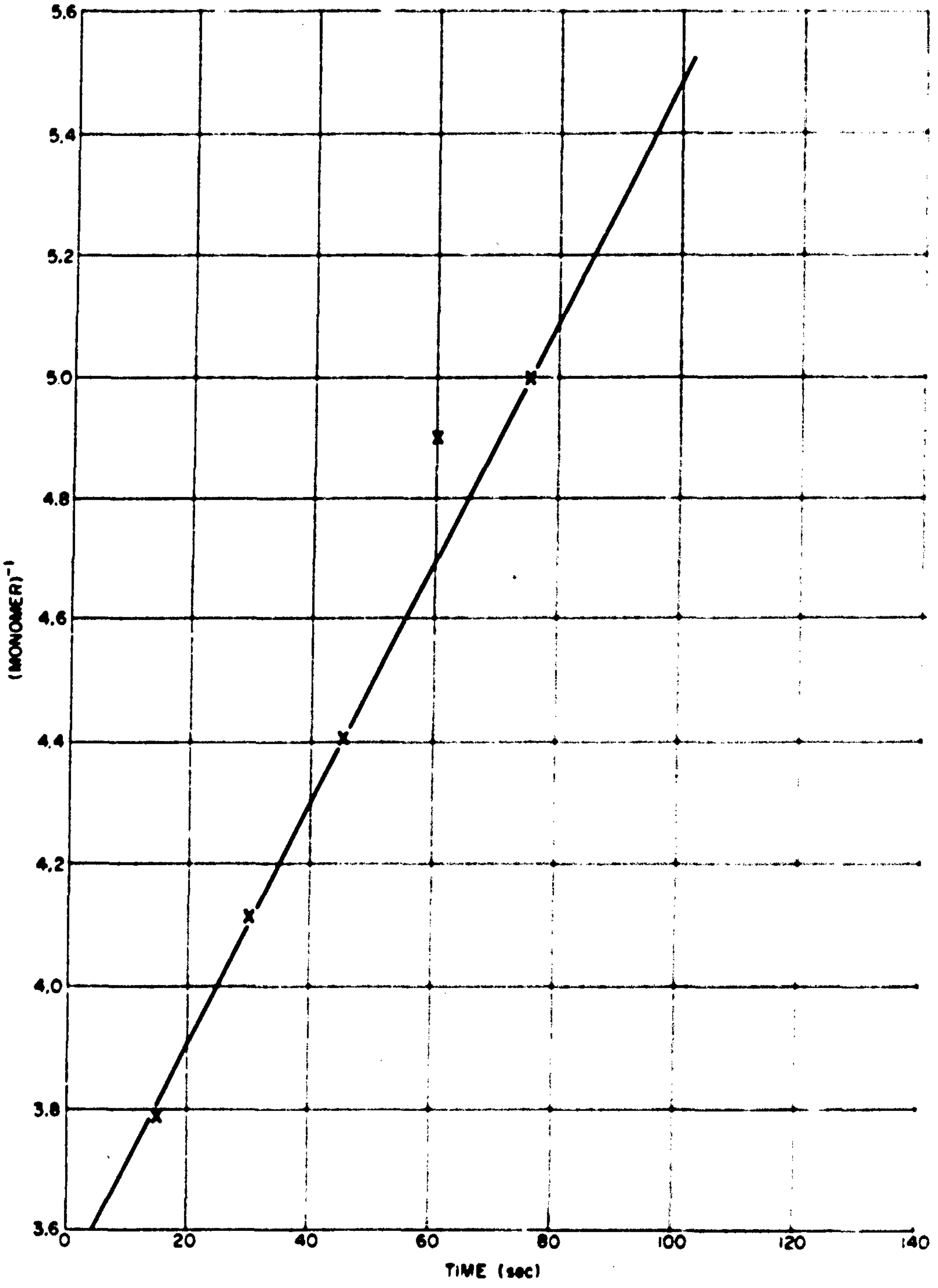

Fig. 4A. Time versus Reciprocal of Monomer Concentration in Polymerization of 0.287 M N-Vinylcarbazole with 0.148 M Diethylchlorophosphate and 0.149 M Water.

content is about three times as high, indicating that the rate of polymerization of N-vinylcarbazole in methylene chloride is inversely proportional to the total water content. A similar comparison of the results shown in Figures 2 and 4 indicates that the rate of polymerization with diethylchlorophosphate is about twice as rapid as that of a polymerization with an equimolar amount of diethylphosphoric acid.

Thus the rate of hydrolysis of diethylchlorophosphate is fast enough for it not to affect the rate of polymerization to a significant extent, hydrochloric acid contributing to the catalysis when it is produced in situ in methylene chloride. This is contrary to previously reported findings regarding the catalytic inactivity of hydrochloric acid when it is mixed with acetonitrile <u>prior</u> to the addition of monomer; whether this is due to reactions of hydrochloric acid with acetonitrile or water prior to reaction with monomer will be established by a similar kinetic study of the polymerization in a mixture of methylene chloride and acetonitrile.

The foregoing results suggest, therefore, that at low conversions, the dependence of the rate of polymerization of N-vinylcarbazole in methylene chloride is given by

$$-d\,[M]/dt = K_o\,\frac{[A]\,[M]^2}{[H_2O]} \qquad (1)$$

where $[A]$ and $[H_2O]$ are the initial concentrations of acid and water respectively and $K_{o(verall)}$ is the overall rate constant for the initiation, propagation and termination processes. This will have to be confirmed by further studies but it is encouraging that there are some similarities between these results and those reported by Brown and Mathieson for the polymerization of styrene with various chloroacetic acids, solvents and water concentrations[1]. In all of the cases studied by them the rate of polymerization was also proportional to the square of the monomer concentration, but the effects of water and catalyst concentrations on the rate depended on the solvent used in the polymerization. They found that in most cases the rate of polymerization was enhanced by increasing amounts of water, at least up to a certain low level of water, after which the rate decreased. Only in one case, a polymerization in nitromethane, was the rate of polymerization proportional to the catalyst concentration and retarded by increasing amounts of water, i.e. dependent on these variables in a manner similar to that which we have observed for the polymerization of N-vinylcarbazole in methylene chloride.

There is one notable, but understandable, difference in the polymerizations of styrene and N-vinylcarbazole catalyzed by Bronsted acids. In the polymerization of styrene with chloroacetic acids, Brown and Mathieson found the carboxylate anion of the catalyst to be rapidly consumed in the polymerization as a result of a chain termination reaction in which the terminal carbonium ion of the polystyrene chain reacts with the carboxylate anion to form a terminal ester group. In a previously reported experiment we found that such a group does not become incorporated in the polyvinylcarbazole chain.

Since the monomer in this case is an amine, it is reasonable to believe that the cationic charge on the proton adducts of monomer and polymer will be concentrated at a nitrogen rather than a carbon atom. Polymerization then results from an induced polarization of the vinyl group attached to a quaternarized amine group. Since carbazole is such a weak base that no salts with acids such as sulfuric acid can be isolated, it is reasonable that no anionic residues of the catalyst were found to be present in polyvinylcarbazole. The apparent lack of catalyst consumption in this polymerization, mentioned earlier in this report, is another indication that the associations of acids with monomer and polymer are extremely weak.

Table I shows, for two time intervals, the measured rates of polymerization, $-d[M]/dt$, and the calculated rates, K_o, based on equation (1), no consumptions of acid and water during polymerization, and complete hydrolysis of diethylchlorophosphate prior to polymerization. In view of the experimental errors likely to be involved in determining conversion, low water contents and delivering proper amounts of reactants, K_o is reasonably constant, confirming the validity of equation (1).

The water concentration and K_o are not indicated for Run 4 in Table I because the water concentration retarding polymerization in this case represents the excess over that required to hydrolyze diethylchlorophosphate. The exact amount of the excess is somewhat uncertain owing to the extreme dependence on the accuracy of the amount of diethylchlorophosphate delivered. The water content before addition of diethyl-

TABLE I

MEASURED RATES AND CALCULATED OVERALL RATE CONSTANT FOR THE POLYMERIZATION OF N-VINYLCARBAZOLE IN METHYLENE CHLORIDE WITH VARYING CATALYTIC CONDITIONS AND MOISTURE CONTENT AT TWO TIME INTERVALS[a]

Run[b]	Time (sec)	$[M]$	$\frac{-d[M]}{dt} \times 10^4$[c]	$[H^+]$	$[H_2O] \times 10^3$	$K_{overall} \times 10^5$[d]
1	30	0.328	7.72	0.149	1.78	8.52
1	45	0.315	7.96	0.149	1.78	9.59
2	30	0.370	8.14	0.149	1.78	7.10
2	45	0.355	8.67	0.149	1.78	8.23
3	30	0.410	3.07	0.149	5.56	6.82
3	45	0.406	2.79	0.149	5.56	6.32
4	30	0.243	14.54	0.296[e]	f	f
4	45	0.227	13.39	0.296[e]	f	f

[a] Data is taken from polymerizations shown in Figs. 1-4. Concentrations of reactants are expressed in moles/l.

[b] Run Nos. correspond to Fig. Nos.

[c] Observed rate in moles/l sec.

[d] Calculated overall rate constant in l./moles sec.

[e] Assuming $[H^+] = 2\ [(C_2H_5O)_2P(O)Cl]$

[f] See text below.

chlorophosphate was about 101% of that required to hydrolyze the catalyst to make the residual water content after hydrolysis 1.78 x 10^{-3} moles/l as in the polymerization with diethylphosphoric acid. It is difficult, however, to control the delivery of a small amount of diethylchlorophosphate (undiluted to minimize hydrolysis prior to addition) to within fractions of 1%. It was calculated that K_o would be 14.81 and 15.61 respectively for the 30 and 45 secs. polymerizations with diethylchlorophosphate (Run 4 in Table I) if there was 0% error in the amount of diethylchlorophosphate delivered to achieve the desired residual water content. It is doubtful that no experimental error was involved. A 0.5% excess in the amount of delivered diethylchlorophosphate would have reduced the residual water content to 1.04 x 10^{-3} moles/l, in which case K_o would be 8.64 and 9.13 respectively for the 30 and 45 sec intervals of Run 4 in reasonable accord with K_o calculated for the polymerization with diethylphosphoric acid. Since a reasonable experimental error can, in this case, cause large variations in the amount of water involved in the calculation of K_o, no useful purpose is served by this calculation under present conditions.

It may be possible to minimize this critical experimental error and its effect by dissolving diethylchlorophosphate in a diluent with a known low water content prior to addition to monomer solution and taking into account the water content of the diluent and resulting hydrolysis of catalyst prior to contact with monomer solution. For the present, however, we believe the view that hydrolysis is involved in the catalysis by diethylchlorophosphate is supported by a comparison of the observed rates of the diethylphosphoric acid and diethylchlorophosphate catalyzed polymerizations and previously reported findings.

The kinetics of the polymerization change at higher conversion as indicated by Figures 1, 2 and 4. In the region where conversion begins to level off the rate of polymerization is also proportional to the square of the monomer concentration. Although it appears interesting, we have not attempted to interpret the kinetics at high conversion in detail since, in view of the application of this polymerization, we are mainly concerned with the conditions affecting the onset of polymerization.

Brown and Mathieson[1] found the variations in the effects of catalyst and water concentrations on the rate of polymerization of styrene with chloroacetic acids to depend mainly on the dielectric constant of the solvent medium. In addition, the rate of polymerization generally increased with dielectric constant. Our experience with the polymerization of N-vinylcarbazole in methylene chloride and acetonitrile indicates that the rate of this polymerization is similarly enhanced by an increase in the dielectric constant of the solvent medium. Although, due to a much faster rate, we do not have detailed kinetic information about the polymerization of N-vinylcarbazole in acetonitrile, there are some qualitative findings and reasons for believing that the dependence of the polymerization rate on catalyst and water concentrations in acetonitrile may be the same as that for polymerizations in methylene chloride, contrary to what might be expected from the findings of Brown and Mathieson[1] regarding effects of solvent polarity on polymerization.

Some of the polymerizations in acetonitrile described in previous reports indicated that the conversion within certain time intervals increases with increasing catalyst and decreasing water concentrations. It seems reasonable to expect the critical aspects to involve the extent to which proton associations with monomer and polymer are upset by competing associations with water and solvent. Although, for an amine, N-vinylcarbazole is a weak base, it is probably a stronger base with respect to protons than either methylene chloride or acetonitrile. The solvating effect of a solvent with a high dielectric constant is likely to favor the formation of cationic adducts of proton with monomeric and polymeric N-vinylcarbazole and reduce the association of such cations with gegen-anions. It is reasonable to believe that these considerations can account for the faster rate of polymerization in acetonitrile. We plan to obtain more detailed information about the influence of dielectric constant on the dependence of the rate of polymerization on catalyst and water concentrations by using a mixture of acetonitrile and methylene chloride as the solvent medium and comparing the results with those obtained with methylene chloride.

A reasonable implication derived from combining our findings with those of Brown and Mathieson[1] is that the rate of polymerization is likely to always depend on the square of the monomer concentration regardless of the solvent medium. This may have important practical application. It suggests it might be possible to make a very sensitive detection device by boosting the monomer concentration, particularly if the remaining part of equation (1) or a more favorable equation is valid for a practical solvent system. In practice, the catalyst and water concentrations are likely to be very small in comparison with the monomer concentration, and if, furthermore, as in equation (1), the rate of polymerization is dependent only on the first powers of the water and catalyst concentrations, it ought to be possible to reduce their quantitative effect on the rate considerably, possibly to the point of insignificance, by maximizing the monomer concentration. About 30 wt. % N-vinylcarbazole can be dissolved in acetonitrile. There may be other suitable solvents in which more monomer can be dissolved. Or, possibly, serious consideration ought to be given to making a more soluble monomer, e.g. an asymmetrical alkyl substituted N-vinylcarbazole, or, possibly, a liquid N-vinylcarbazole by attaching a long and suitably branched alkyl group to one of the aromatic rings of this monomer, which could be polymerized in the absence of solvent.

These suggestions are based on considerations involving the overall kinetics as indicated by equation (1) for the initiation, propagation and termination processes. Although it seems unlikely at the present time, there is a possibility, however, that water or the water/catalyst ratio is critical, for instance, in the initiation stage, in which case special precautions to minimize the water content may have to be taken. In a disposable detection device it may be possible to accomplish this by covering the polymerization system with a layer of a finely divided molecular sieve material around a window through which to observe polymerization. A material such as Linde 3A sieves might be suitable because it absorbs only the smallest molecules such as water and, possibly, hydrogen chloride. For the moment, however, there would seem to be no need to be overly concerned about this possibility, since the following experiment suggests that polymerization can occur when the concentration of water is much higher than that of catalyst.

In an attempt to observe polymerization with a minimum amount of catalyst, 0.1 ml of a freshly prepared solution of 4×10^{-8} g diethylchlorophosphate in dry methylene chloride (<5 ppm H_2O) was added to 1 ml. of a freshly prepared solution of 0.25 g. freeze-dried N-vinylcarbazole in dry acetonitrile (<5 ppm H_2O) in an unbaked and unstoppered test tube (it was found previously that water content is not affected significantly by atmospheric exposure and using unbaked tubes in these tests). This tube was placed next to one containing a similar control solution of monomer containing no diethylchlorophosphate. An easily seen turbidity appeared in the solution containing diethylchlorophosphate within 13-14 minutes. This test was repeated several times and the result was reproducible until the test solutions became spoiled for reasons not fully understood at present. Tests with lower concentrations of diethylchlorophosphate were not attempted.

Although the polymerization with this trace of catalyst still appears to be too vulnerable to environmental conditions for it to be considered a demonstration of practical feasibility on which a development of a detection device might be based, the test does demonstrate an inherent capability of this polymerization to detect minute quantities of catalytic agents. It is likely that the concentration of catalyst involved in this test is the lowest ever known to catalyze any polymerization. The catalyst concentration is of an order of magnitude similar to that which is generally believed to be the concentration of transition states in organic reactions, implying a low activation energy for the polymerization in acetonitrile, consistent with what is generally known about ionic polymerizations. The test also provides a further indication that catalyst is not consumed in the polymerization and, also, that polymerization is not inhibited by a high water to catalyst ratio. Although all reagents were thoroughly dried it is reasonable to assume that even with the best drying procedures it is not possible to reduce the water content to anywhere near the catalyst concentration that was used.

Whether the effect on polymerization shown in Fig. 4 of the in situ formation of hydrogen chloride from diethylchlorophosphate in methylene chloride could also be expected to be present when acetonitrile is used as the solvent remains to be determined in a similar kinetic study of the polymerization in a mixture of acetonitrile and methylene chloride. Regardless of the outcome, however, atmospheric hydrogen chloride could still not be expected to be quite as effective a catalyst as diethylchlorophosphate or a similarly hydrolyzable agent since the polymerization with hydrogen chloride would be retarded by water present in solution and water would be consumed in the hydrolysis of an agent such as diethylchlorophosphate.

The millivolt readings shown in Table II were obtained with a Leeds and Northrup pH meter in what turned out to be a rather poor attempt to correlate the relative catalytic activities of acids with the acidities they produce in acetonitrile. In the previous report it was shown that trifluoroacetic acid is a more potent polymerization catalyst than diethylphosphoric acid, and some of our recent qualitative observations indicate that acetic acid is a still weaker catalyst. The order of these catalytic activities appears to correlate with the relative "acidities" produced by these acids in acetonitrile according to the results shown in Table II.

This correlation might not be affected by at least one of the obvious discrepancies shown in this Table. The spectroquality acetonitrile distilled from P_2O_5 which was used in this experiment appears to contain an acidic impurity. The presence of such an impurity was also indicated by a "spontaneous" polymerization which was found to occur in this batch of acetonitrile when monomer with a low water content was added. It is believed that the impurity might be a trace of acetic acid

TABLE II

POTENTIOMETRIC READINGS (MILLIVOLT SCALE) PRODUCED BY INSERTION OF ELECTRODES OF A pH METER INTO VARIOUS GRADES OF ACETONITRILE IN THE ABSENCE AND PRESENCE OF VARIOUS SOLUTES

Solvent and Solutes	Initial	After 3-1/2 Hours
reagent grade acetonitrile	+268	+253
spectroquality acetonitrile	+17	+85
distilled spectroquality acetonitrile (P_2O_5)	-175	-48
0.076 M diethylphosphoric acid in distilled acetonitrile	-337	-341
0.075 M trifluoroacetic acid in distilled acetonitrile	-445	-481
0.175 M acetic acid in distilled acetonitrile	-209	-162
0.175 M acetic acid in spectroquality acetonitrile	-118	-102
0.559 M water in distilled acetonitrile	-208	-131

produced by hydrolysis of acetonitrile as a result of the presence of a small amount of water in spectroquality acetonitrile and a catalyst such as P_2O_5 or H_3PO_4. The effect is not due to atmospheric carbon dioxide, since a repeat of a previous test confirmed that carbon dioxide does not catalyze polymerization.

The impurity problem was unexpected because distillation from P_2O_5 appears to be the most widely used laboratory method for purifying and drying acetonitrile, e.g. in connection with conductivity investigations. The problem has been solved, however, by passing acetonitrile distilled from P_2O_5 through a column of powdered CaH_2 and this procedure is now being used as a precautionary measure in drying and purifying this solvent (curiously, in the case of acetonitrile, distillation from CaH_2 is not nearly as effective a drying procedure as distillation from P_2O_5). We will recheck the acidities of various acids in acetonitrile.

We will also retest the stability of N-vinylcarbazole in wet acetonitrile, since the same contaminated acetonitrile was involved in a test in which N-vinylcarbazole was stored in acetonitrile containing 5000 ppm water. This solution remained clear and stable for two weeks, but the impurity might have caused premature destabilization.

A search for less volatile polar solvent media for the polymerization of N-vinylcarbazole was begun. A slow polymerization occurred in unpurified glutaronitrile (Eastman white label) and none occurred in unpurified dimethylsulfoxide (Baker, reagent grade) with diethylchlorophosphate as the catalyst. A number of solvents of this type will be distilled and tested.

PLANNED WORK

For the near future we plan to determine the activation energy for the acid catalyzed polymerization of N-vinylcarbazole in methylene chloride, and to make a kinetic study of the homogeneous polymerization in a mixture of methylene chloride and acetonitrile. By comparing the kinetics of the polymerizations in methylene chloride and in mixtures of this solvent with acetonitrile, we hope to establish whether increasing the dielectric constant of the solvent medium, in addition to increasing the rate of polymerization, affects the dependence of the rate on catalyst, water and monomer concentrations, and whether the previously observed deactivation of the catalytic properties of premixed hydrogen chloride is due to reaction with acetonitrile or moisture in the solvent. If a reaction with acetonitrile is responsible, the rates of polymerization with equimolar amounts of diethylchlorophosphate and diethylphosphoric acid would be expected to be the same when a mixture of solvent is used. If reaction with water is responsible, the relative difference in the rates of polymerization with these catalysts should be the same as that found when methylene chloride is used as the sole solvent. We will continue a search for a suitable, but less volatile, polymerization solvent, and combine and evaluate all the information obtained in this program to determine the most promising reaction conditions for a detection system.

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