

The Thermal Decomposition of Poly(vinylidene Chloride) in the Solid State

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Synopsis

The rate of decomposition of PVDC is sensitive to differences in the method of preparation of the polymer. Polymers prepared by mass polymerization of very pure monomer were most stable. Emulsion polymerized PVDC degraded the fastest. The activation energy for the latter was 34.4 kcal/mole. Over the range of 130°–190°C, the rate of decomposition increases with reaction time to ~10% HCl evolved. Beyond this point, the reaction follows first-order kinetics. The first-order rate is independent of molecular weight. Lamellar crystals of PVDC degrade at a higher rate than "as polymerized" powders. This may be due in part to annealing of the crystals in the degradation temperature range; but it also results from a sensitization of the polymer to thermal degradation from exposure to the polar solvents used for recrystallization. A mechanism is proposed to account for these observations.

INTRODUCTION

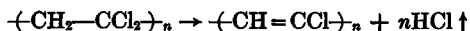
An investigation of the solid-state thermal decomposition of poly(vinylidene chloride) (PVDC) has been carried out. The objective of this study was to evaluate the role of polymer morphology in the degradation mechanism. Below its melting point ($T_m = 200^\circ\text{C}$), PVDC degrades to an unsaturated crosslinked residue by eliminating HCl. The polymer does not fuse during this process, and its morphology appears to be retained in the degraded products. This implies that the reaction takes place in the solid state. It is to be expected that morphology will be an important variable in any solid state process.

PVDC is normally obtained in the form of a crystalline powder directly from the polymerization reaction. The polymer particles are complex aggregates with a well-developed lamellar substructure. The morphology can be influenced both by changing polymerization conditions and by recrystallization from dilute solution.¹ Polymers obtained by low-conversion mass polymerization have a very high degree of crystallinity, small particle size, and high surface area. Suspension polymers, on the other hand, are somewhat lower in crystallinity and are obtained as spherical particles 20–50 μ in diameter. The particles obtained by crystallization from dilute solution have a folded-chain lamellar structure with thicknesses on the order of 40–80 Å.

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Polymer morphology was not specifically considered in the early work on degradation. The basic mechanism for the decomposition was first proposed by Boyer² and elaborated upon in studies by Matheson and Boyer³ and by Havens.⁴ Extrapolating from the studies of Marvel et al.⁵ on PVC, they proposed a two-step mechanism:

1. Chain-reaction elimination of HCl to form poly(chloroacetylene) sequences:



2. Condensation between conjugated sequences to form crosslinked polymer.

They also examined the role of chemical reagents and radiation in the degradation process. Basic solvents like morpholine and transition metal salts catalyzed the decomposition. Havens also detected HCl catalysis under certain conditions.

The essential correctness of this mechanism was demonstrated by the work of Winslow and co-workers⁶ who studied the stepwise pyrolysis of PVDC gravimetrically.

They found in agreement with Boyer et al. that below 190°C, only the first reaction was significant. They attributed further dehydrochlorination between 190° and 350°C to Diels-Alder condensation followed by elimination. The structure of PVDC was destroyed in the first part of the decomposition. The x-ray diffraction pattern after 65% HCl loss resembled that of crosslinked polystyrene.

At about the same time, Tokareva et al.⁷ reported a limited kinetic study over the temperature range 140°–170°C. Although their data indicated autoacceleration from the beginning of the decomposition, they analyzed the results in terms of a zero-order process. They found the activation energy to be 33.6 kcal/mole. Oxygen was observed to increase the rate. They proposed a radical chain reaction mechanism to account for the results.

Dacey and co-workers⁷ began an investigation of the carbonization of PVDC in 1953, which later included kinetic studies.^{9,10} They followed weight loss of pelletized polymers while holding in a nitrogen atmosphere and examined the products by infrared spectroscopy. They concluded that, below 190°C, the reaction was first order with an activation energy of 28 kcal/mole. The appearance of IR bands in the 1500–1700 cm⁻¹ region indicated formation of conjugated double bonds. The intensity of these bands increased up to ~50% HCl loss and diminished at higher extents of reaction. These results are also in agreement with the two-step reaction mechanism.

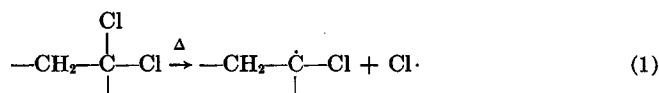
Burnett and co-workers^{11–14} studied the initial part of the decomposition under high vacuum in the range 130°–180°C. They noted that the polymer became yellow and insoluble at ~1% HCl loss. Infrared analysis detected isolated double bonds at this point. Conjugated double bonds appeared only at 5% HCl loss.

They analyzed the kinetics as a zero-order process even though their data, like that of the Russian workers, was not very linear except over a short interval. They found an activation energy of 30 ± 1.5 kcal/mole. The initial rate in the solid state was found to be inversely related to molecular weight. Burnett et al. proposed a free-radical mechanism initiated at chain ends. The presence of radicals in the reaction was later confirmed by Hay¹⁵ using ESR spectroscopy.

Bailey and Everett first reported in 1966 that there was a connection between the morphologies of PVDC and the resulting carbonized product.¹⁶ This theme was elaborated upon in a following paper.¹⁷ They found that if degradation was carried out below 190°C, the polymer morphology was largely retained indicating that the crystalline solid is decomposed without softening. The polymers studied had lamellar structures with thicknesses of ~ 100 Å. The carbon particles had a similar appearance but the thickness was increased to 200–500 Å. They suggested that this was due to cross-linking between lamellae during degradation.

Everett et al.^{18,19} found the reaction to be first order after an induction period of accelerating rate. They could find no molecular weight dependence but did observe an effect of particle size on the kinetics. Their data suggested, however, that this was not a simple surface area effect but rather was related to some other morphologic characteristic associated with particle size.

The evidence pointed to a free-radical chain reaction initiated at the particle surface. Based on the assumption of a folded-chain lamellar crystal structure for PVDC, Everett et al. proposed the following mechanism: a monomer unit in a chain fold is more reactive because of steric strain. It dissociates thermally into a radical pair as shown by eq. (1):



The local chain conformations determine whether the chain radical crosslinks by coupling with a neighboring fold or whether the chlorine radical initiates a chain reaction that propagates into the crystal. This mechanism yields a crosslinked poly(chloroacetylene) product containing trapped radicals. The latter serve to initiate Diels-Alder condensation when the temperature is raised above 200°C.

Though this mechanism is in qualitative agreement with the data reported in the literature, it leaves many questions unanswered. The reaction is catalyzed by reagents that clearly do not act by a radical mechanism. The wide variations in the results reported by various workers suggest that the kinetics may reflect varying levels of impurities in the polymer samples. The exact role of morphology has not been defined. Since it varies with mode of polymerization, this might explain differences in reported data, such as the wide variation in values of the activation energy. In addition,

early results from our degradation studies indicated that annealing during the degradation process was also an important factor.²⁰

Annealing can take place in the range 130°–160°C before degradation becomes serious. In analogy with what we know about other polymers, this probably represents a thickening of the lamellar polymer crystals. Annealing does not take place at room temperature and appears to start somewhere in the vicinity of 100°C. At lower temperatures, PVDC appears to degrade only at the surface of the crystals whether the degradation is caused by aging,¹⁸ UV exposure,¹⁹ or exposure to basic solvents.²² The onset of annealing appears to be associated with the alpha-transition T_α . This is the temperature at which chains within the polymer crystal begin to absorb energy; T_α for PVDC is $\sim 80^\circ\text{C}$.²⁵

EXPERIMENTAL

Polymer Preparation

The emulsion polymers were prepared by a continuous-addition emulsion polymerization technique.²¹ Molecular weight was varied by changing temperature and *tert*-butyl hydroperoxide level. Conversions were above 90%. The latexes were freeze coagulated, washed free of soap, and dried in vacuo at 40°C. Data on these samples are given in Table I.

The mass polymerizations were carried out at various temperatures. Monomer was distilled directly into the polymerization vessel under a nitrogen atmosphere. After polymerization, the samples were washed free of unreacted monomer and freeze dried from cyclohexane suspension in order to get fluffy powders. Some samples were isolated and dried in the polymerization tubes without exposing the polymer to the atmosphere. The degradation experiments were then carried out on these polymers while still in the polymerization tube. This procedure was designed to eliminate any possibility of contamination by dust or oxygen. Data on the mass polymers are listed in Table II.

Another series of polymers was prepared by polymerizing VDC in various solvents. This is a slurry rather than a solution polymerization since

TABLE I
Emulsion Polymers

Sample no.	Polymerization temperature, °C	Particle size, Å	$[\eta]$, dl/g ^a
E1	25	955	0.577
E2	25	995	0.765
E3	20	865	0.800
E4	20	955	0.930
E5	20	—	0.962
E6	20	940	1.1 ^b

^a In tetramethylene sulfoxide at 25°C.

^b Estimated from initiator level.

TABLE II
Mass Polymers

Sample no.	Polymerization temperature, °C	Initiator	Concentration, moles/mole	Conversion, %
M1	20	IPP ^a	3.2×10^{-4}	12.8
M2	20	IPP	1.5×10^{-4}	7.9
M3	25	AZO ^a	2.0×10^{-4}	6.2
M4	25	UV	—	<20
M5	70	BZ ₂ O ₂ ^a	3.2×10^{-4}	49.4

^a Isopropyl percarbonate, azobisisobutyronitrile, and benzoyl peroxide, respectively.

TABLE III
Solvent Polymerized Polymers

Sample no.	Solvent	Temperature, °C	Initiator
S1	cyclohexane	25	AZO
S2	cyclohexane	20	IPP
S3	benzene	20	IPP
S4	<i>o</i> -dichlorobenzene	25	AZO
S5	bromochloromethane	25	AZO
S6	dioxane	20	IPP
S7	cyclohexanone	20	IPP
S8	methanol	25	AZO
S9	methanol/H ₂ O	20	IPP

PVDC is not soluble in the reaction media. The usual conditions were 10% to 20% by volume monomer in solvent, ~0.2% initiator, at 20°–25°C in a slowly stirred reactor. The reactions were limited to low conversions, <20%. The systems used to make samples are listed in Table III. The solution polymers were recovered by washing free of unreacted monomer and freeze drying either from the solvent used or from cyclohexane.

Polymer Decomposition Experiments

The polymer powders were degraded thermally under high vacuum. The sample was weighed into a tube and connected to a high-vacuum manifold, and the system was preevacuated to 5×10^{-3} torr. To start the decomposition, the evacuated tube was connected to the trap and immersed in a silicone oil bath regulated to the desired temperature. Glass joints subjected to the high temperatures were sealed with Apiezon black wax. A Fisher proportional controller was used to maintain the bath at $\pm 0.1^\circ\text{C}$ of the desired temperature.

The evolved HCl was collected in the U-tube trap by cooling the latter in liquid nitrogen. The amount of HCl collected was measured intermittently by evaporating it into a calibrated flask and measuring the pressure.

Some of the degradations were carried out at atmospheric pressure by passing a stream of dry nitrogen through the tube. The HCl gas was trapped in a water bath and titrated intermittently with standard caustic solutions.

Intrinsic Viscosity

Intrinsic viscosities were run on solutions made up by weight in hexamethyl phosphoramidate. Bath temperature was $25.0 \pm 0.02^\circ\text{C}$. Flow times in Cannon-Ubbelohde viscometers were measured with a Mechrolab automatic viscometer apparatus. A minimum of three points were obtained for each sample; $[\eta]$ was determined by a standard extrapolation to zero concentration.

Melting Points

Melting points of the powders were measured on a du Pont 900 DTA. Samples were heated in a 4-mm tube under N_2 at $30^\circ\text{C}/\text{min}$. The melting points given are the temperatures of the main endotherm.

RESULTS

A large number of samples were screened to see how wide a variation in thermal stability existed. They were degraded at 160°C both under N_2 and under vacuum. They encompass a wide range of molecular weights, particle size, and endgroup structure. These samples were degraded in a relatively short time after preparation to minimize aging effects. The results in Table IV show no correlation either with preparative method or molecular weight.

The kinetics of dehydrochlorination of several mass polymers were studied at 160°C . These polymers, having been prepared with various kinds of initiators, were expected to show whether endgroup structure is an important factor. A plot of HCl evolved as a function of time at 160°C is shown in Figure 1. The only significant difference between these samples is in the duration of the initial period of accelerating rate.

During the initial period, the rate increases to a maximum. As further reaction takes place, the rate falls slowly, approaching zero at ~ 12.3 meq HCl evolved per gram ($\sim 60\%$ decomposition). The same data are replotted as $\log [1 - (\text{HCl}/\text{HCl}_0)]$ in Figure 2. The plots are linear from the end of the initial period up to $\sim 40\%$ decomposition. The average first-order rate constant calculated from the slope of this plot is $4.7 \times 10^{-3} \text{ hr}^{-1}$.

Any differences in rate of decomposition for times beyond the initial period are within experimental error. These rates obtained under high-vacuum conditions are the same as the rate of decomposition under 1 atm N_2 of a high molecular weight polymer.²⁰ The initial rates do not agree with the data of Burnett et al. on either the lowest or the highest molecular weight samples in their series. The results for the intermediate molecular weights, however, are quite close.

TABLE IV
Comparison of the Thermal Stability of PVDC Samples at 260°C

Sample no.	T_m , °C	$[\eta]$, dl/g	HCl loss in 24 hr, %	Initial rate, ^a meq HCl/(g hr)
E1	200	0.58	25.5	0.25
E2	201	0.77	—	0.26
E3	199	0.80	24.6	0.24
E4	199	0.93	26.8	0.26
E5	199	0.96	—	0.24
E6	199	1.1	—	0.26
M1	—	—	20.9	0.18
M2	—	—	—	0.19
M3	200	1.02	20.6	0.17
M4	200	—	21.5	0.19
M5	—	—	—	0.07
S1	200	0.24	21.7	—
S2	202	—	33.5	0.31
S3	201	—	33.0	0.37
S4	199	0.28	26.3	—
S5	—	0.32	31.2	—
S6	200	—	23.6	0.17
S7	201	30.0	—	0.49
S8	199	0.14	32.0	—
S9	200	0.59	—	0.21

^a Averaged over initial 10%.

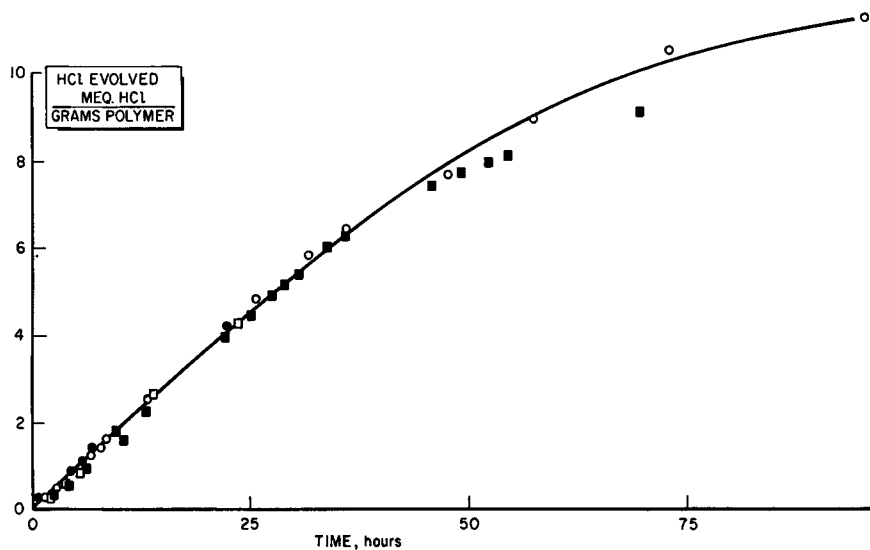


Fig. 1. Thermal decomposition of poly(vinylidene chloride) at 160°C. Composite curve for four mass-polymerized samples.

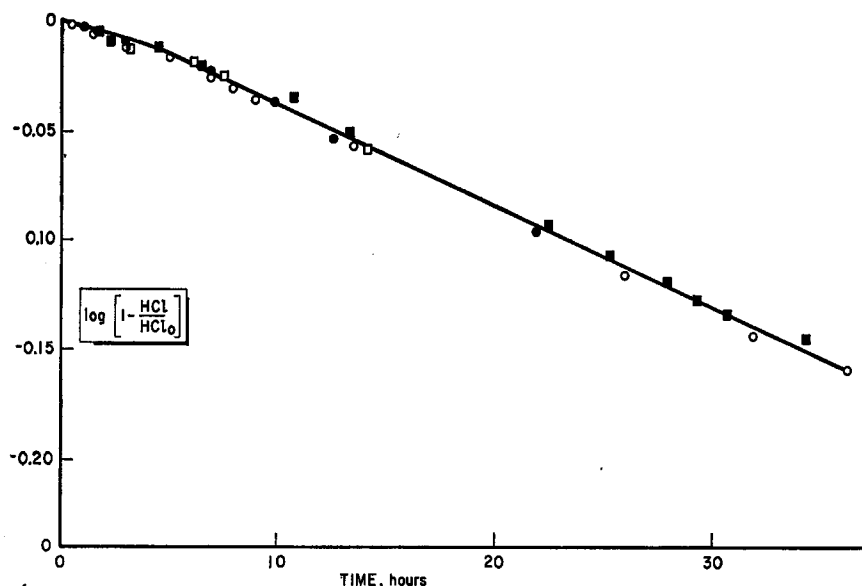


Fig. 2. Analysis of the kinetics of thermal dehydrochlorination. First-order plot of the data from Fig. 1.

The recipes used for mass polymerization should have yielded high molecular weight polymers. A spot check showed that sample M3 had an intrinsic viscosity $[\eta] = 1.02$ dl/g. Sample M2 was not isolated, but a polymer prepared under similar conditions had a value $[\eta] = 0.532$ dl/g. The high molecular weight polymer degraded under N_2 had a value of $[\eta] = 1.90$ (in tetramethylene sulfoxide), showing that the range of molecular weights used in Burnett's study was not drastically different.

Since a change in initiator can influence both molecular weight and end-group structure, a direct comparison was made using the same initiator at different levels. Two samples were prepared at low temperature (20°C) with IPP as initiator. Precautions were taken to avoid any possible contamination. The samples were degraded under high vacuum without prior exposure to the atmosphere. Both sets of data fall on the curve in Figure 1; doubling the initiator concentration had no effect either on the duration of the initial period or on the first-order rate constant.

A further study was made on the effect of molecular weight using a series of samples made by emulsion polymerization. The results are shown in Table V. The induction times, i.e., the initial period of accelerating rate, seem to increase slightly with molecular weight.

In a related series of experiments, samples of polymer E4 were degraded to various degrees at 160°C and then tested for solubility in hexamethylphosphoramide. The undegraded polymer dissolves easily in this solvent at room temperature.²⁰ After 0.98% of the HCl in the polymer was eliminated, HMPA solubility was markedly decreased. The polymer was ex-

TABLE V
Kinetic Data on Emulsion-Polymerized Samples

Sample no.	$[\eta]$, dl/g	Initial rate, meq/(g hr)	Induction time, hr	First-order rate coefficient, $\text{hr}^{-1} \times 10^3$
E1	0.58	0.25	0.8	5.6
E3	0.80	0.24	1.2	5.6
E4	0.93	0.26	1.4	5.7
E6	1.1	0.26	1.8	5.6

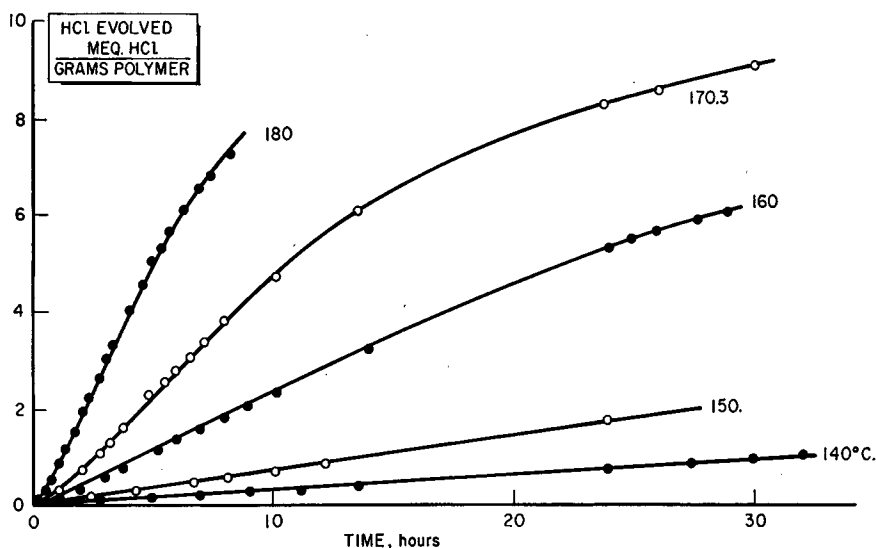


Fig. 3. Effect of temperature on the thermal dehydrochlorination of emulsion-polymerized poly(vinylidene chloride).

tensively swollen, but very little of the sample dissolved. After 4.3% reaction, the polymer was insoluble and swelled only slightly. After 11.2% reaction, the polymer was not appreciably swollen by HMPA. These experiments were carried out in the absence of oxygen, showing that insolubilization was induced by degradation rather than by postoxidation of the degraded polymer.

The effect of temperature on the kinetics was also studied with emulsion polymers. The results for sample E1 are shown in Figure 3. The rates are not constant, except possibly at 140°C, but the extent of decomposition in this case is really too small to make a judgment. The linear region on a log plot is shorter than for mass polymers extending only to $\sim 25\%$ reaction. It does not appear that the 140°C sample actually degraded beyond the induction period; but in the other cases, the induction period seems to decrease with temperature or at least fall to a minimum value.

The high molecular weight latex polymer, E6, showed essentially the same behavior as E1. The rate constants were the same within experi-

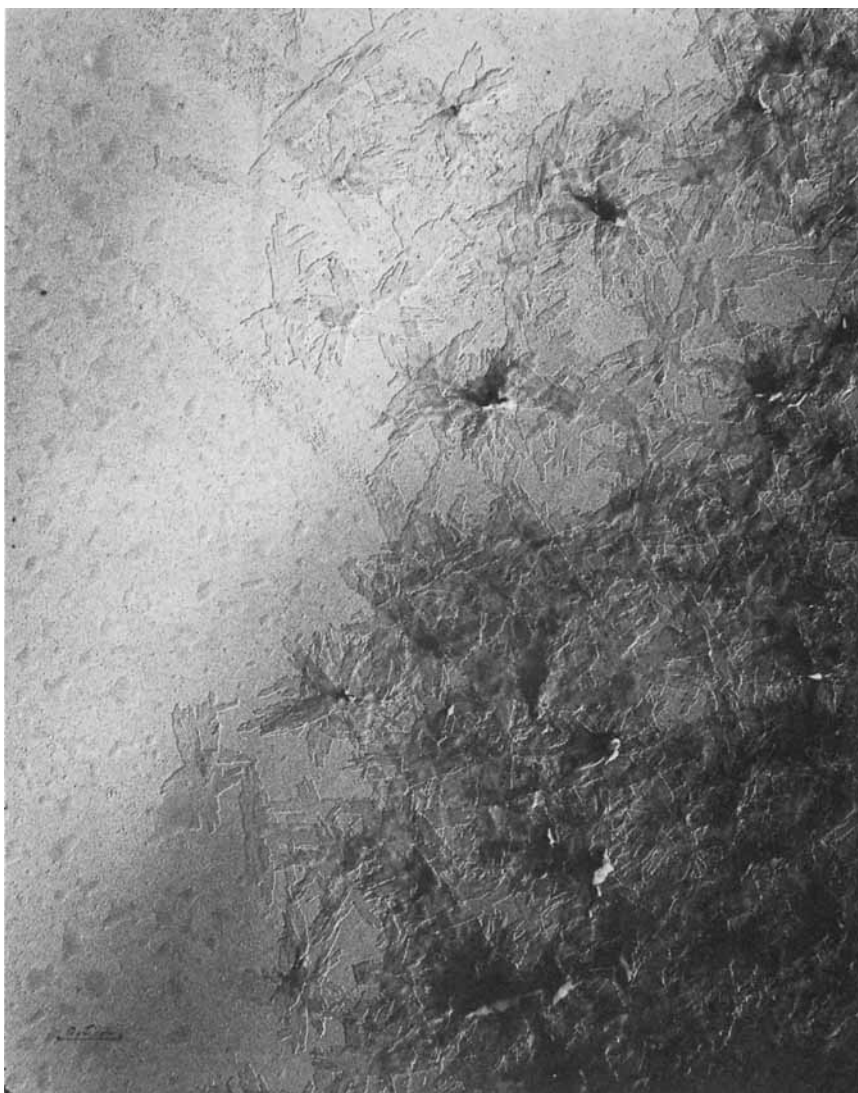


Fig. 4. Electron micrograph of PVDC lamellar crystals grown from tetrahydrothiophene at 25°C.

mental error, but the induction periods were slightly longer as noted before. The activation energy obtained from an Arrhenius plot of the rate constants is 34.4 kcal/mole (average for E1 and E6).

The rate constants for the emulsion polymers averaged $\sim 5.6 \times 10^{-3} \text{ hr}^{-1}$ at 160°C. This is significantly higher than the value obtained for the mass polymers ($4.7 \times 10^{-3} \text{ hr}^{-1}$). The poorer stability could be caused by the initiator (*t*-BHP) or the latex particle morphology, but it seems more likely that it results from a slight amount of hydrolysis of the polymer that takes place during polymerization. Though these polymers had nearly

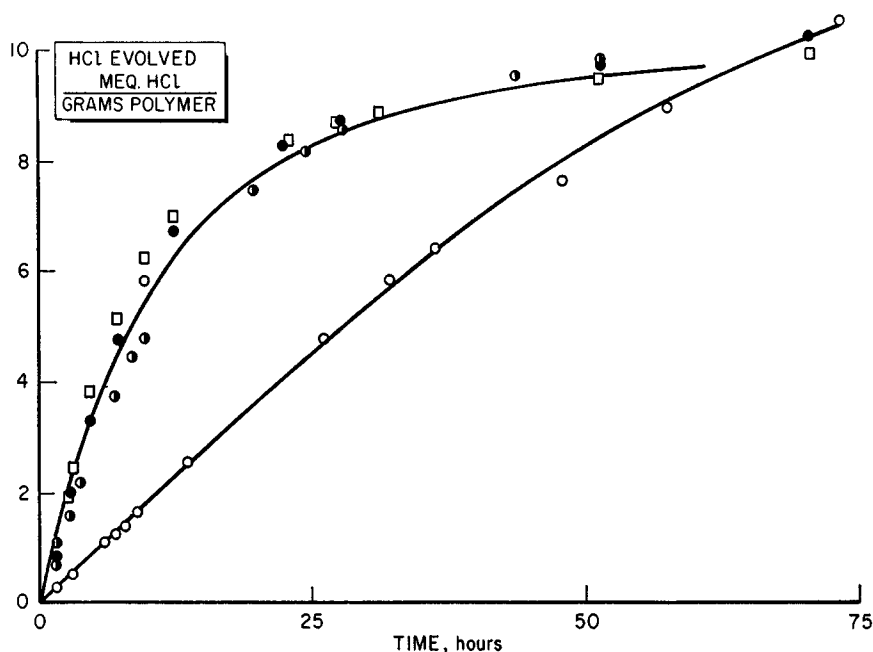


Fig. 5. Thermal decomposition at 160°C of PVDC recrystallized from tetrahydrothiophene: (O) as-polymerized sample M4; (●) $T_c = 40^\circ\text{C}$; (□) $T_c = 25^\circ\text{C}$; (○) $T_c = 0^\circ\text{C}$.

theoretical chlorine content, they were slightly yellowish in color in comparison to the "snow white" mass polymers. This difference carried over into solutions, indicating that it was not simply a light-scattering effect that made one polymer look whiter than the other.

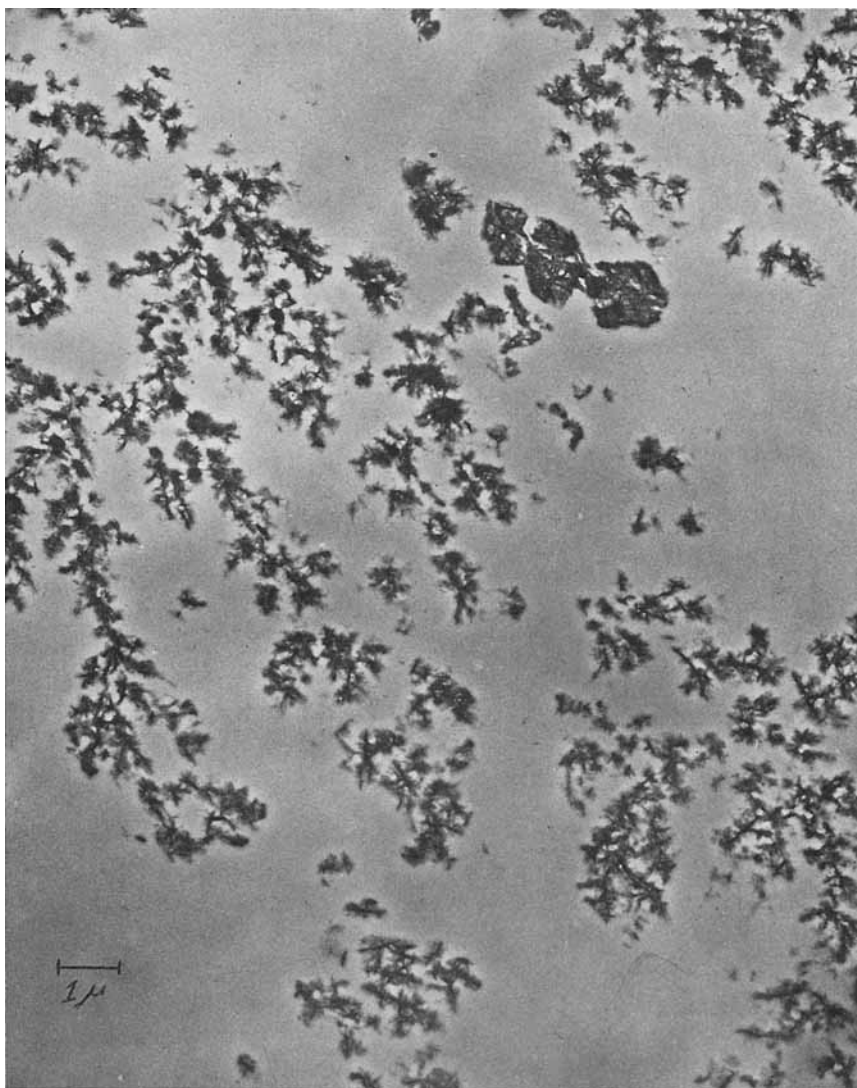
To further explore the possible effect of powder morphology on the kinetics, two approaches were tried. In one case, lamellar polymer crystals were prepared by recrystallizing PVDC from dilute solutions; and, in the other approach, vinylidene chloride was polymerized in a series of solvents known to yield powders with markedly different morphologies.¹

Recrystallization was attempted from several solvents. The first experiments were carried out in cyclopentanone, a solvent that had been used before to obtain lamellar crystals.²² Crystals grown at 73°C in this solvent were severely discolored upon isolation and decomposed rapidly when heated. The same result was obtained by recrystallizing from cycloheptanone, a slightly better solvent, at 60°C. What appeared to be undegraded crystals were finally obtained by recrystallization from dilute solutions in tetrahydrothiophene at 0°, 25°, and 40°C; this system was shown earlier to give good results.²⁰ Even in this solvent, crystals grown at 60°C were discolored. Electron micrographs obtained in conjunction with the present study indicate that crystals with the desired lamellar structure were obtained.²³ A typical example is shown in Figure 4.

The crystals were washed, dispersed in benzene, and freeze dried to avoid compaction. The fluffy powders were devolatilized at 10^{-3} torr before

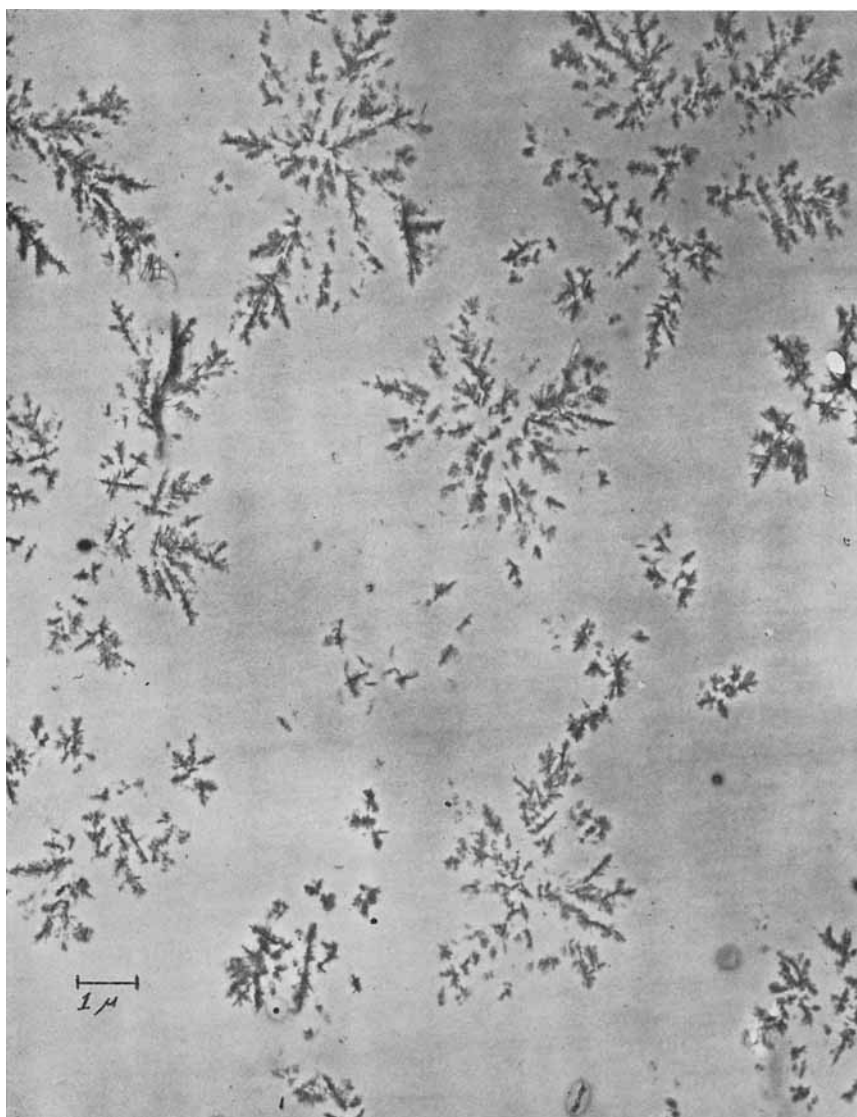
degrading at 160°C. The results are shown in Figure 5. In comparison with the original sample, this treatment greatly increased the rate to ~ 1 meq/(g hr). Within experimental error, crystallization temperature has little effect on the decomposition kinetics. This is probably the result of a leveling effect brought about by solvent-induced degradation.

Similar problems were encountered when studying the degradation of "as polymerized" PVDC. The differences in morphology between a mass polymer and polymers prepared by slurry polymerization in a solvent medium are shown in Figure 6. These micrographs show cross-sectional



(a)

Fig. 6. (continued)



(b)

Fig. 6. (continued)

views of "as polymerized" powders embedded in epoxy resin and sectioned by the method of Traylor and Garrett.²⁴

No correlation could be identified between polymerization medium and rate of degradation, as is apparent from the data in Table IV. As the HCl evolution curves in Figure 7 show, both of the slurry polymers degrade faster than mass polymer. Surprisingly, the polymer prepared in cyclohexane, a nonpolar medium, is more unstable than mass or emulsion PVDC. The difference between the cyclohexane polymer and the mass polymer does



(c)

Fig. 6. Comparison of the morphologies of PVDC powders; particles embedded and sectioned; transmission electron micrographs: (a) polymerized in mass; (b) polymerized in cyclohexane; (c) polymerized in cyclohexanone.

not appear to be due to morphologic differences; the particle shapes, sizes, and surface areas are similar. In the case of powders with very different morphology prepared in cyclohexanone, the rate of decomposition was also higher.

Neither attempt to demonstrate the effect of morphology on degradation gave very satisfactory results owing to the poor reproducibility of the HCl

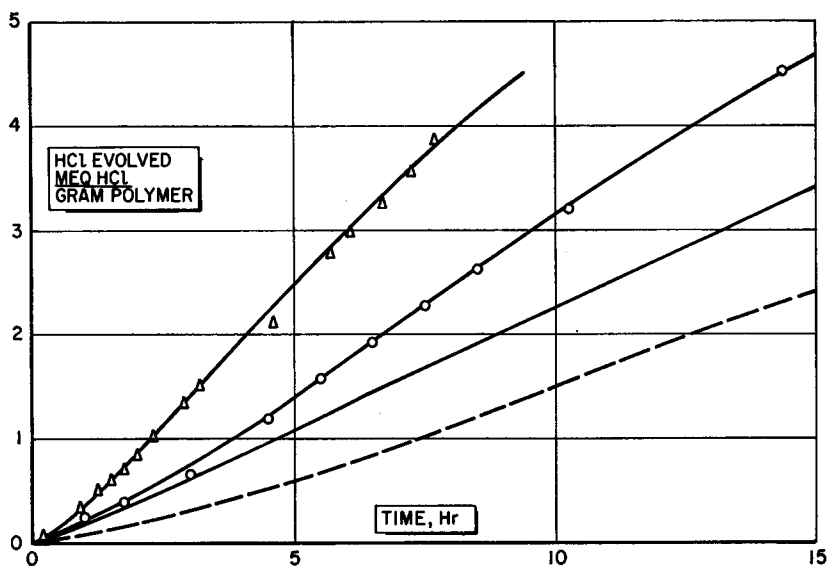


Fig. 7. Thermal decomposition of PVDC; comparison of polymers prepared in different media: (Δ) cyclohexanone; (O) cyclohexane. Solid curve, emulsion polymer; dashed curve, mass polymer.

evolution data. This seems to be related to variable degrees of instability induced in the polymer as a result of preparative conditions. This was particularly evident in polar solvents which apparently attack PVDC even at room temperature. The net effect is much like that observed in the emulsion-polymerized samples, no obvious degradation but sensitization to subsequent thermal degradation.

DISCUSSION

The reaction shows an initial period of increasing rate followed by a region in which first-order kinetics are observed. The activation energy found in this study lies at the high end of the wide range of values reported previously (28–33.6 kcal/mole). Approximately 10% of the total available HCl is evolved in the initial or "induction" period. Another 20–40% is released in the first-order region. The rate drops to very low values at higher extents of reaction.

Zero-order kinetics represent only the initial part of the reaction. Assuming that poly(chloroacetylene) is the only product, the reaction based on extent of conversion to that product is first order from 20% to 80% conversion.

In contrast to the results of Burnett et al.¹¹ our data indicated no dependence of rate on molecular weight. Everett et al.^{18,19} made the same

observation and suggested that the inconsistency was due to differences in the range of molecular weights studied by Burnett et al. But the intrinsic viscosities reported in all of these studies cover a comparable range. Another explanation is that polymers made with benzoyl peroxide initiator have endgroups that influence the initial reaction (which was the only region investigated by Burnett et al.), but not the first-order rate region.

These differences may also reflect changes in polymer morphology. The conditions used by the various workers to prepare their polymers would produce significant morphologic differences. But our attempt to define this aspect in more detail was frustrated by the fact the techniques used to effect morphologic variation also produced other more subtle changes. In particular, contact of the polymer with polar solvents seems to sensitize it to thermal dehydrochlorination. This may be due to the formation of trace amounts of activating species such as carbonyl groups and double bonds.

The same difficulty prevented isolation of the role of annealing. Nevertheless, it would appear that the connection between annealing and bulk degradation is more than coincidental. Degradation throughout the polymer crystal does not occur below the annealing temperature range. We propose that the initial period of accelerating rate arises as a consequence of the interaction between the annealing process and the dehydrochlorination reaction. The polymer crystals are thickening during annealing and, in the absence of degradation, would reach a thickness characteristic of the annealing temperature. But at the same time the polymer is undergoing simultaneous dehydrochlorination and crosslinking.

As suggested by Everett et al., the reaction probably originates in the chain-fold regions on the polymer crystal surface. Though they proposed a free-radical initiation step, a unimolecular polar elimination like that suggested for PVC²⁶ is a real possibility. The apparent ease with which PVDC is sensitized to thermal degradation by basic reagents suggests a polar initiation mechanism. Recent studies by Davies and Henheffer²⁷ have shown that the activation energy for dehydrochlorination reaction of PVDC dissolved in hexamethyl phosphoramide is the same as that observed for the solid-state thermal decomposition. Grant²⁸ has presented convincing evidence that PVDC degrades by an ionic E2 elimination process in this solvent.

The above observations together with the results of the present study suggest that the dehydrochlorination chain reaction initiates from double bonds formed on the surface of the crystal by a polar elimination. If the latter is the rate-determining step as proposed by Laurent et al.²⁹ for solution degradation, then a connection between kinetics and morphology becomes apparent.

Following the suggestion of Harrison and Baer²² that the rate of primary dehydrochlorination is determined by the chain-fold conformation, it appears that the number of such conformations must increase with time

initially to account for the early acceleration. This implies that the initiating site is a tight fold since the concentration of the latter presumably increases with annealing time.

At the temperature where thermal degradation of PVDC is commonly studied, surface double bonds would readily react either by dimerization or bimolecular initiation with an adjacent methylene group. The free radicals generated in the process could initiate radical-chain reactions propagating into the crystal.

These reactions are taking place as the crystals anneal. The fold length of the lamellar crystals increases with $\log t$ during the annealing process.³⁰ Since thickening and crosslinking occur at the same time, a point must eventually be reached where further thickening is blocked by immobilization of the polymer chains. (An analogous effect is well known in the case of polyethylene single crystals. Annealing is completely suppressed by radiation crosslinking of the crystal surfaces.³¹) Once the morphology is frozen in by crosslinking, the pattern of decomposition must change. We suggest that this point correlates with the end of the period of accelerating rate. Further decomposition of the crosslinked crystals follows apparent first-order kinetics.

In the mechanism described above, the rate is dependent both on the rate of formation of primary double bonds and on the number of repeat units degraded per initiation. The initial reaction in this mechanism should be most sensitive to factors like morphology and molecular weight. The higher the molecular weight, the more rapidly the polymer will become immobilized. How this would affect the kinetics is not completely clear, though the data in Table V indicate that the induction period is lengthened.

The first-order rate should be less affected by starting morphology and molecular weight. It should be very sensitive, however, to lamellar thickness at the point where the crystals become rigid. The thinner the crystal at this point, the greater the number of folds. Therefore, if the decomposition of the latter to form double bonds is the rate-determining step, thin crystals should decompose most rapidly. This could explain in part the observed results with recrystallized specimens where the lamellar thickness was less than that of "as polymerized" PVDC.

The above analysis puts into better focus the many aspects of the first stage PVDC decomposition. But it also points out the difficulty in trying to study the reaction experimentally. Morphologic changes take place during the decomposition. Therefore, characterization of the polymers before degradation is not sufficient. A further resolution of the problem will require a more detailed understanding of the primary elimination and crosslinking reactions.

The authors benefited from many helpful discussions of this problem with T. Alfrey, Jr., D. S. Gibbs, and Professors H. Morawetz and E. Baer. The polymers samples were prepared by J. L. Townsend and J. H. Oswald. The latter also assisted in the characterization of these materials.

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