perature immediately before making the observation. Isothermal distillation within the apparatus furnishes a very sensitive test for the purity of the liquid. As the result of observations made on acetic acid, bromine, benzene and carbon tetrachloride, it may be concluded that the vapor pressure of a sample of liquid rapidly elevated to the boiling point is identical with that which it exerts after remaining for several hours at the boiling point. Delay in attaining internal equilibrium is therefore not a factor of influence in the measurement of boiling point or vapor pressure of these liquids, and observations may be made as soon as temperature equilibrium is established.

PRINCETON, NEW JERSEY

[CONTRIBUTION NO. 38 FROM THE EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY]

THE KINETICS OF THE POLYMERIZATION OF VINYL ACETATE

BY HOWARD W. STARKWEATHER AND GUY B. TAYLOR

RECEIVED AUGUST 7, 1930 PUBLISHED DECEMBER 18, 1930

Vinyl acetate forms high polymers on heating alone or in solution, with or without a catalyst.[1] The present investigation indicates that the probable mechanism of the process from monomer to polymer is a type of chain reaction.

The rate of polymerization was observed by measuring the contraction in volume. A linear relation was established between percentage contraction on the original volume of the monomer and the degree of polymerization by density measurements and by evaporating mixtures of monomer and polymers to constant weight, the polymers being nonvolatile.

Apparatus

Dilatometers similar to those used in measuring the thermal expansion of liquids were constructed, consisting of bulbs of 18 mm. tubing and approximately 20 cc. capacity, sealed to straight tubes 4–7 mm. in diameter. The straight tubes were graduated in per cent. Those made from the smaller tubing could be read to 0.02% and the larger one to 0.05%. The thermostats for heating the dilatometers consisted of three large tubes equipped with condensers and filled with boiling benzene, water and toluene. The temperatures of the different baths at the position of the dilatometer bulbs as determined by calibrated thermometers were 82, 101 and 111°.

---

[1] H. Staudinger, K. Frey and W. Starck, *Ber.*, **60**, 1782–92 (1927); Whitby, McNally and Galley, *Trans. Roy. Soc. Can.*, **22**, 27–32 (1928). There are also numerous patents on the subject.

Experimental Procedure

The vinyl acetate was distilled, using an ordinary condenser, so that it was exposed to the air. It was kept in a clean tin can to protect it from the light. In some of the measurements the acetate was distilled in vacuum directly into the dilatometer in the all-glass apparatus shown in Fig. 1. The acetate was placed in B and cooled with solid carbon dioxide while the whole apparatus was exhausted with an oil pump. After sealing at E, C was cooled with liquid air or solid carbon dioxide and B allowed to reach room temperature. After collecting a light fraction in C, B was again cooled and D sealed. By a similar procedure another fraction was collected in the dilatometer A, rejecting the heavy fraction left in B. The dilatometer was then sealed off at F.

In experiments with air-distilled vinyl acetate, alone or in toluene solution, air was pumped out of the dilatometer after cooling the acetate to −78°. Since the measurements were made at temperatures above the boiling point of the acetate, it was necessary to use a closed system. In preparing toluene solutions definite volumes of vinyl acetate were run from pipets into weighed 100 cc. graduated flasks. They were then filled up to the mark with toluene at 22°. Within the limits of accuracy of this work, no appreciable change in volume was found upon mixing vinyl acetate and toluene.

After a dilatometer had been filled and sealed it was placed in a water-bath at 22° and allowed to stand until the meniscus position was constant. The dilatometer was then placed in the boiling liquid (water, benzene or toluene) bath and the liquid level was read at frequent intervals. In the absence of an added catalyst the level usually rose for the first three to six minutes and then gradually fell. When a catalyst was present the level frequently started to fall by the end of one or two minutes, and the maximum reading was calculated from the reading at 22° and from the expansion as determined in the absence of the catalyst. The dilatometers in most cases were allowed to stay in the bath until no further contraction took place; this required from one to nine days.

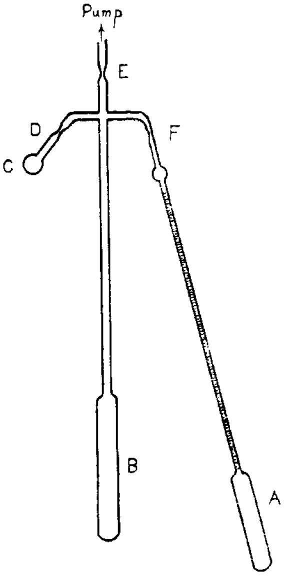

Fig. 1.

Experimental Results

According to Staudinger and others,[1] when vinyl acetate polymerizes it does not yield a single chemical individual but a mixture of polymeric homologous compounds. Our experimental method is justified only if the average density of the mixed polymers is the same throughout the course of the reaction. It is not necessary to treat the reaction product as a chemical individual because we are concerned only with the rate of disappearance of the monomer. Whether the actual densities of all the polymers are nearly the same is not so important in establishing the kinetics of the process as are the differences in density between the monomer and the mixed polymers.

In this study the assumption has been made that all the polymers are non-volatile. In a number of cases, after measuring contractions in the dilatometer, the contents were evaporated to constant weight. Most of the toluene and monomer (b. p. about 60°) were allowed to evaporate at room temperature, and then the sample was kept in a vacuum oven at 65° until it reached constant weight. This required from one to two weeks. The results are given in Table I. Column 4 is calculated from Columns 2 and 3, and Column 6 from Columns 4 and 5. From the table it will be seen that percentage non-volatile (*i. e.*, polymers) is approximately proportional to contraction under widely varying initial concentrations. The experimental error in data of this kind is necessarily high for obvious reasons, but there is no definite trend in the values for percentage polymerization *versus* percentage contraction, so that the average may be accepted.

TABLE I

RELATION BETWEEN VOLATILITY AND CONTRACTION

1	2	3	4	5	6
% by volume of monomer in toluene		Observed % contrac. of soln. at 101°	Calcd. % contrac. in vol. of monomer	% non-volatile on orig. wt. of monomer	% polymerization per % vol. contrac. of vinyl acetate at 101°
At 22°	At 101°				
20	20.55	1.41	6.86	24.5	3.57
		2.83	13.76	46.5	3.38[a]
		3.36	16.35	55.8	3.41[a]
40	40.81	5.28	12.94	45.5	3.52
		9.85	24.14	87.3	3.62[a]
		9.66	23.67	85.2	3.60[a]
60	60.81	12.34	20.29	81.7	4.03
		14.15	23.26	90.1	3.88[a]
		14.39	23.65	91.9	3.89[a]
80	80.56	17.55	21.80	79.6	3.65
100	100	11.16	11.16	43.3	3.88
		19.60	19.60	67.4	3.44
				Average	3.65

[a] Reaction catalyzed with benzoyl peroxide.

From this average, 3.65%, the contraction corresponding to complete polymerization is 27.4%. From density measurements of monomer and polymer at 101°, the calculated contraction is 26.8%, in fair agreement with the above figure of 27.4%. Since determinations of density could be made much more accurately than of non-volatile matter, contractions used in interpreting the data were calculated from them at all three temperatures. Table II gives the measured densities and the contraction calculated from the densities for complete polymerization. As an example of the calculation: 100 g. containing 61.6 g. monomer, at 82°, occupies $100/0.834 = 120$ cc., the monomer $61.6/0.85 = 72.5$ cc., the polymer $61.6/1.142 = 53.9$ cc. The contraction is $(72.5 - 53.9)/120 = 15.5\%$.

Table III summarizes some of the data obtained. The time in minutes

TABLE II

CONTRACTION DUE TO POLYMERIZATION

% monomer in toluene By vol. at 22°	By wt.	82° Density	82° Contraction, %	101° Density	101° Contraction, %	111° Density	111° Contraction, %
20	21.1			0.798	5.48		
60	61.6	0.834	15.5	.809	16.25	0.798	16.5
80	81.0			.815	21.5		
100	100	.850	25.6	.823	26.8	.812	27.2
Polymers		1.142		1.125		1.116	

is given for each 10% reaction. Results obtained with pure vacuum-distilled vinyl acetate were easily reproducible, but those with the air-distilled material varied appreciably. The reaction with the pure acetate was allowed to proceed at all three temperatures until no more contraction in volume occurred. The densities of the three products thus obtained were determined by weighing in water and air at room temperature and found to be 1.190 ± 0.002. The uniformity in density indicates the same mixture of reaction products at all three temperatures.

TABLE III

RATES OF POLYMERIZATION OF VINYL ACETATE

% by vol.	Temp., °C.	Time in minutes to reach indicated % polymerization 10	20	30	40	50	60	70	$k \times 10^4$
				Vacuum-distilled					
100	82	100	230	375	530	725	1000	1320	11
100	101	20	45	75	112	157	205	261	53
100	111	7.5	16	25	36	49	68	102	140
60	82	200	500	930	1470	2200	..	..	5
60	101	40	88	162	272	400	675	1580	26
60	111	17	40	75	120	200	380	760	62
				Air-distilled					
100	101	5.5	12	19.5	28	40	56.5	88	191
80	101	13	34	65	115	185	320	580	81
60	101	32	105	175	320	600	1340	..	33
20	101	800	3000	[a]	..	..	..	..	..
				1% Benzoyl peroxide					
60	101	..	..	4	..	..	9	16[b]	
20	101	4	8	15	26	49	131	[c]	

25% in 90 hours. [b] 88% in 16 hours, then no reaction next 3 hours. [c] 61% in 3 hours, then no reaction next 24 hours.

The rate of polymerization of pure vacuum-distilled vinyl acetate approximately follows the law for a unimolecular reaction. Table IV gives the complete data for the run at 101°. The constant, k, was calculated from the formula

$$k = \frac{1}{t} \ln \frac{c}{c - x}$$

where c is the contraction for complete polymerization and x the contraction at time t.

TABLE IV

POLYMERIZATION OF VACUUM-DISTILLED VINYL ACETATE AT 101°

Time, minutes	Dilatometer scale	Contraction, %	$k \times 10^4$
0	126.5[a]	...	
2	142.2	...	
3[b]	142.45	0	
8	141.5	.67	50
14	140.4	1.44	50
20	139.3	2.21	51
26	138.2	2.98	51
31	137.4	3.55	51
50	134.6	5.52	49
62	132.9	6.71	49
81	130.5	8.39	48
106	127.7	10.36	47
154	124.1	12.88	43
222	118.5	16.81	45
309	113.2	20.54	48
414	107.4	24.61	61
∞	...	26.8	

[a] At 22° before placing in boiling water jacket. [b] Taken as zero time in computing velocity constant.

Undiluted vinyl acetate gives a fair unimolecular constant in all cases over the entire range. The temperature coefficient for 10° is 2.7 and the heat of activation 25,000 calories, which is the same order of magnitude as for other high-polymer reactions given by Kienle.[2] In toluene solutions the computed values for k fall rapidly with time. For example, take the case of the 80% solution at 101°, the constants figured for each 10% reaction up to 50% are 81, 66, 55, 44, 37 $\times 10^{-4}$. The values of k given in Table III for the toluene solutions are figured for the first 10% reaction, merely as an index of relative speeds at the start.

The effect of benzoyl peroxide upon the rate of polymerization of the 20% solution of vinyl acetate in toluene at 101° is shown in Fig. 2. The rate curves between 190 and 1200 minutes are omitted from the figure. After 1200 minutes, Samples II and III were cooled and more of the peroxide was added. After being replaced in the boiling water-bath, the polymerization rates increased sharply, as shown by the curves. The 1% additional benzoyl peroxide added to Sample II after 1200 minutes gave a curve practically identical in slope with that obtained with Sample V, which contained 1% of the peroxide at the start. In the first 1200 minutes Sample III, containing ten times as much catalyst as Sample II, polymerized only half again as much, and Sample V with 50 times

---

[2] R. H. Kienle, *Ind. Eng. Chem.*, **22**, 590–594 (1930).

something over twice as much. The curves show, in general, that a given amount of catalyst causes the same degree of polymerization, whether added all at once or in portions at successive time intervals.

In no case did the reaction in toluene solutions go to completion although in some experiments the heating was continued for nine days. It is perhaps significant that in the uncatalyzed reactions the polymerization of 40, 60 and 80% solutions apparently stopped when they contained approximately 2.0 moles of monomer per liter, while the polymerization of the 20% solution appeared to stop when it contained 1.5 moles of monomer per liter.

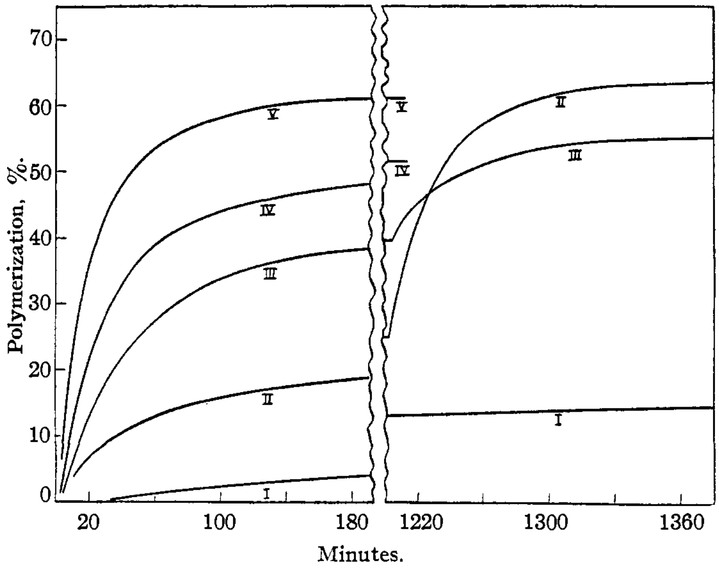

Fig. 2.—Polymerization of 20% vinyl acetate in toluene (101°). Percentage of benzoyl peroxide: I, 0.00; II, 0.02 and 1.0; III, 0.2 and 0.2; IV, 0.4; V, 1.0.

There are negative as well as positive catalysts for this polymerization. A sample of air-distilled vinyl acetate containing 1% of sulfur was heated for twenty hours in boiling water with no detectable contraction in volume. If no sulfur had been added, polymerization would have been essentially complete. This effect of sulfur had been determined previously by Blaikie.[3]

Discussion of Results

It seems likely that we are dealing with a chain reaction of some kind. The reaction involves the combination of many molecules to form a polymer and yet it follows the unimolecular reaction rate law. The explana-

---

[3] Blaikie, Canadian Patent 282,860 (1928).

tion is probably similar to that put forward by Christiansen and Kramers[4] to explain a simpler type of pseudo-unimolecular reaction. In this theory an activated molecule is formed for every one that reacts.

Benzoyl peroxide acts as a trigger catalyst in starting reaction chains and is itself destroyed in the process, since chemical tests always showed its absence when the catalyzed reaction stopped. Anti-catalysts, like sulfur, interrupt the reaction chains. The inhibition of the reaction by toluene may be explained on the basis that activated molecules give up their energy to the toluene molecules before they can combine with other vinyl acetate molecules. In other words, the toluene has the same effect in breaking reaction chains that walls exhibit in some homogeneous gas reactions.

Summary

The polymerization of pure vinyl acetate is shown to follow the unimolecular rate law. In toluene solution the rate of reaction is retarded. The kinetics of the polymerization are explained on the basis of a chain reaction. Benzoyl peroxide acts as a trigger catalyst by initiating reaction chains. Sulfur inhibits the reaction.

WILMINGTON, DELAWARE

[COMMUNICATION NO. 439 FROM THE KODAK RESEARCH LABORATORIES]

THE VACUUM FRACTIONATION OF PHLEGMATIC LIQUIDS

BY K. HICKMAN AND W. WEYERTS

RECEIVED AUGUST 7, 1930 PUBLISHED DECEMBER 18, 1930

In the course of some work on heavy oils the need has been encountered for an adjective which will convey the sense of "difficultly volatile" or "high boiling." Instead of inventing a word we have prepared to adapt a word which is already well known and, therefore, nearly self-explanatory. Such a word is "phlegmatic." Derived from the Greek φλεγματικός, the original suggestion of "fieryness" has given place to the well-accepted sense of sluggishness, apathy or resistance to disturbance. *Phlegmatic* seems a particularly suitable word to denote high-boiling properties, and it is the adjective which will be used throughout this paper.

Many separations of phlegmatic liquids by fractional distillation could be performed more efficiently or more conveniently[1] at very low pressures if it were not for the uncertainty concerning the real pressure in the distilling

---

[4] Christiansen and Kramers, *Z. physik. Chem.*, **104**, 451 (1923). See also Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Clarendon Press, Oxford, 1929, Chapters V and VI.

[1] Bumping vanishes entirely at pressures below 1 mm.