Polymerization Activity Test for Vinyl Chloride

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Synopsis

A polymerization activity test has been developed for evaluating the purity of commercial vinyl chloride. A 40-g. portion of vinyl chloride is heated with 0.500 g. of benzoyl peroxide for 2 hr. at 70°C. in a glass liner in a stainless steel autoclave, and the weight of the polymer formed determined. The effects of the heat transfer medium in the autoclave, time, oxygen, limited agitation, catalyst concentration, and temperature on the percentage conversion of monomer to polymer were determined. The effect of acetaldehyde, crotonaldehyde, chloroprene, 1,1-dichloroethane, *trans*-1,2-dichloroethylene, paraldehyde, and 1,1,2-trichloroethane on the conversion and the molecular weight of the polymer are described.

A convenient, rapid, and safe polymerization activity test for vinyl chloride, which is both reproducible and sensitive to the known impurities in commercial monomer, does not appear to exist. The so-called soda or Coke bottle emulsion polymerization test, which is sometimes used industrially, has several serious drawbacks. The test is hazardous and requires a relatively long time to carry out, i.e., 10–15 hr., since the bottle is made of soft glass and must be cooled and heated up very slowly. The test is usually carried out to a relatively high conversion, e.g., 85%. At this percentage conversion, the time–conversion curve is relatively flat and differences between samples are minimized. Furthermore, no provision is made to ensure complete removal of oxygen from the bottle prior to polymerization even though oxygen is known to have a serious effect. Also, since there are at least three ingredients besides the monomer present in the polymerization mixture, differences in results are inevitable when new supplies of these materials are used. In our laboratory, great differences in polymerizations have been observed due to subtle differences in the purity of the catalyst, water and protective colloid. Hence, it was decided to try to develop a test using a simpler polymerization system which could be carried out in a commercially available, low-priced autoclave.

A small commercial stainless steel autoclave fitted with a Pyrex liner which is recommended for ASTM procedure D525 was used. A diagram of the apparatus is given in Figures 1 and 2. The capacity of the glass liner was 125 ml. A weight of 40 g. of monomer was chosen for the test for the following reasons. On adding 40.00 g. of water to the autoclave (weighing 3600 g.), it was found that the weight of the water could be determined on a
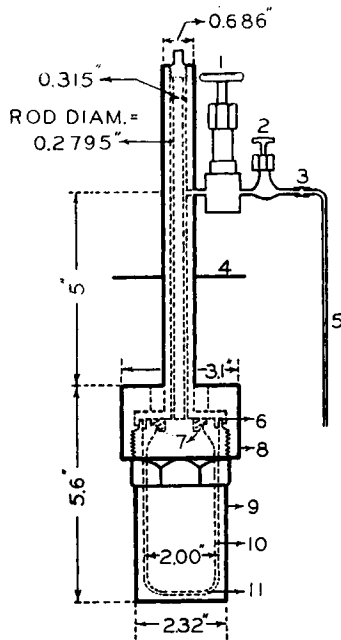
Fig. 1. Diagram of apparatus for polymerizing vinyl chloride: (1) $^1/_8$ in. 18-8 stainless steel needle valve; (2) $^1/_8$ in. brass Hoke needle valve; (3) rubber connection; (4) supporting plate; (5) glass capillary tube, 2 mm. I.D. × 160 mm.; (6) composition gasket; (7) stainless steel ring (cf. Fig. 2); (8) top section of stainless steel autoclave; (9) bottom section of stainless steel autoclave; (10) glass liner; (11) mercury, 18 ml.
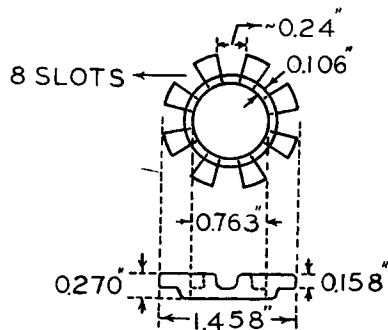

Fig. 2. Stainless steel ring to force glass liner into pool of mercury.

Keller balance (10 kg. capacity) with a deviation of ±0.5%. This was within acceptable limits. Furthermore, 40 g. of vinyl chloride would fill somewhat less than half the glass liner, thus leaving adequate free space.

Heat Transfer Medium

Several dozen orienting polymerizations were first carried out to define approximately the conditions necessary to give maximum sensitivity to

impurities with adequate reproducibility. There was also a stipulation that the total time required for the test should not exceed 3–5 hr. It was apparent at once that if no heat transfer medium was put between the glass liner and the autoclave, conversions would be impractically low. Hence, various liquids were tried. The results are summarized in Table I. In each test, 40 g. of vinyl chloride and 1.000 g. of benzoyl peroxide were heated for 60 min. in a stationary autoclave immersed in a stirred water bath at 70°C. An 18-ml. portion of heat transfer agent was used, which was sufficient to immerse most of the liner. The maximum reaction temperature was measured with a maximum mercury thermometer placed in the polymerizing mixture.

TABLE I
Effect of Heat Transfer Medium on the Conversion of Vinyl Chloride to Polymer

Sample no. of monomer	Heat transfer medium	Conversion to polymer, %	Max. temp., °C.
1	None	5.7	57
1	G.E. silicone oil	20	—
1	Silicone DC 704	17.1	63.7
4	D.C. silicone grease	18.6	68.8
4	D.C. Silicone Antifoam A	23.5	70.5
2	Mineral oil (Klearol)	21.8	59.7
2	Mineral oil (Nujol)	28.4	68.7
4	Hydrocarbon (Octoil-S)	25.5	69.2
3	Aroclor 1254	15.7	64.7
3	Aroclor 1242	10.0	59.7
4	Dioctyl phthalate	19.3	64.1
4	Di(isodecyl) phthalate	20.8	65.9
4	Di(tridecyl) phthalate	24.4	70.0
4	Di(tridecyl) phthalate + 0.25% bisphenol A	21.9	66.0
4	Di(tridecyl) adipate	20.0	66.0
4	Dioctyl azelate (commercial)	25.2	70.2
5	Dibutyl sebacate (redistilled)	17.1	63.5
4	Ucon Oil LB550 X	23.2	68.1
4	Redistilled mercury	32.2	69.8
5	Redistilled mercury	28.0	68.9

The silicones were nonvolatile and did not creep up the walls of the autoclave. General Electric silicone and DC 704 imparted a characteristic odor to the autoclave suggesting a slight reaction with vinyl chloride and/or decomposition. D.C. silicone grease (regular viscosity), which is a solid at room temperature, gave a rate of heat transfer which was not altogether reproducible. D.C. Antifoam A appeared to be the most satisfactory silicone. All of the high boiling hydrocarbons (i.e., Klearol, Nujol, Octoil-S) crept up the walls of the autoclave and contaminated the polymer. The Arochlors appeared to inhibit polymerization. Of the phthalates, di(tridecyl) phthalate, which had been washed free of stabilizer (bisphenol

A), gave the highest conversion. A trace of the phthalate crept up to the top of the autoclave and may have got into the polymer. The lower phthalates gave lower conversions and more creeping. Di(tridecyl) adipate did not creep but gave a relatively low conversion. Commercial dioctyl azelate crept very much while dibutyl sebacate crept slightly. Ucon oil LB550 X (a polypropylene oxide) gave somewhat erratic conversions possibly due to the presence of peroxides. Redistilled mercury gave the highest conversion without contamination of the polymer and hence was chosen as the heat transfer medium. However, the conversion decreased if the same portion of mercury was used repeatedly.

Effect of Time on Conversion

With a bath temperature of 70.0°C. (corr.), a benzoyl peroxide concentration of 2.5%, and mercury as the heat transfer medium, the results given in Table II were obtained. It is apparent that the curve begins to deviate substantially from a straight line between 2 and 4 hr. Hence, the duration of polymerization should not exceed about 2 hr. in order to maintain maximum differentiation between samples.

TABLE II
Time–Conversion Curve for Vinyl Chloride

Duration, hr.	Conversion to polymer, %
1	28.4
2	51.8
4	66.4

Effect of Oxygen

The exit tube of the autoclave is supplied with a rod to reduce the free space. With the rod in the exit tube, conversions were very much more reproducible than without it. This suggested that residual traces of air (which would be lower with the rod) influenced the rate of polymerization. With the rod in position, conversions were usually 43.0–44.6% at a bath temperature of 80°C., a reaction time of 1 hr., and a benzoyl peroxide concentration of 1.25%. To reduce the residual oxygen, the autoclave (with rod in position) was partially and rapidly evacuated with a water ejector as described in the experimental section. On cooling the charge with liquid nitrogen and measuring the residual permanent gas with a McLeod gage, the pressure was found to be substantially less than 0.1 mm. Hg absolute. Its conversion was almost the same as that obtained without evacuation with the rod in position. When the charge was first evacuated with a water ejector and then with a mercury diffusion pump to a pressure of 0.03 mm. Hg absolute (after being cooled with liquid nitrogen), the conversion obtained was 44.5%. It was thus apparent that when the rod was in the exit tube and the autoclave partially evacuated with a water ejector, the

charge was sufficiently oxygen-free to give reproducible results. The deliberate addition of 0.05–0.1% of oxygen, calculated at operating conditions, was found to have no effect.

The effect of adding a relatively large concentration of oxygen to the charge was also studied under the final conditions adopted for this activity test (i.e., benzoyl peroxide concentration 1.25%, bath temperature 70°C., duration of polymerization 2 hr.). When the autoclave was partially evacuated as described in the experimental section, the conversion averaged 36.2%. When the autoclave was cooled to −78°C. after evacuation and about 500 mm. Hg of air allowed to enter by suction, the conversion increased to 52 ± 1%. Also the maximum temperature increased from the usual value of 67–68°C. to 85°C. The polymer was grey or pinkish grey rather than the usual white. This same conversion was obtained when the concentration of benzoyl peroxide was increased from 1.25 to 2.5% at 70°C.

Effect of Lid on Glass Liner and Limited Agitation

The glass liner is ordinarily supplied with a glass lid. When the lid was placed on the liner, a considerable proportion of the polymer at the bottom of the liner was black while most of it at the top was white. It was suspected that this was due to local overheating due to poor agitation. However, insertion of a glass bubbling tube such as those used in the boiler of a vacuum distillation made no difference either to the color of the polymer or the percentage conversion of monomer. Hence, the use of both bubbler and lid was discontinued. No further attempts to agitate the charge were made since the polymer was white, and apparently homogeneous, without it.

Effect of Catalyst Concentration and Temperature on Reproducibility

The optimum conditions for an activity test are that combination of lowest catalyst concentration and lowest polymerization temperature which will give maximum sensitivity to the presence of impurities while at the same time maintain adequate reproducibility. There are also practical limitations as to the total length of time allowed to carry out the test. In this case, a limit of 3–5 hr. was set. This would allow a maximum duration of polymerization of about 2 hr. From the preliminary experiments, it was apparent that a temperature of 70–80°C. would have to be used in order to remain within this limitation. Therefore, one series of experiments was carried out at 70°C. and another at 80°C. at various concentrations of benzoyl peroxide. The results are summarized in Table III. The average mean deviation values are only of semiquantitative significance, since deviations due to factors in technique steadily decreased as the investigation proceeded. However, it was apparent that at 80°C. the concentration of benzoyl peroxide could be reduced to 0.625% without an excessively great increase in deviation. Lower concentrations were not tried as a further increase in the deviation would not have been acceptable. Simi-

TABLE III

Effect of Catalyst Concentration and Temperature on Reproducibility

Sample no.	Bz₂O₂ concn., %	Bath temp., °C.	Duration of polymerization, hr.	Conversion (avg.), %	% Avg. mean deviation	No. of expts.
1	2.5	80	1	40.5	4.4	4
2	1.25	80	1	42.9	4.0	5
3	0.625	80	1	34.7	6.7	4
1	2.5	70	1	27.9	5.1	7
1	2.5	70	2	51.8	4.1	3
2	1.25	70	2	35.4	3.3	6
2	0.625	70	2	22.7	—	1

larly, at 70°C. the concentration of benzoyl peroxide could be reduced to 1.25%.

Optimum Temperature

To determine whether a temperature of 80°C. with a catalyst concentration of 0.625% and a duration of polymerization of 1 hr., or a temperature of 70°C. with a catalyst concentration of 1.25% and a duration of 2 hr. would give greater sensitivity to impurities, polymerizations were run under both sets of conditions. A multi-gallon charge of crude vinyl chloride produced from acetylene and hydrogen chloride was distilled batchwise in a commercial column, and six approximately equal fractions were taken off. From previous work it was known that virtually all the by-products boil higher than vinyl chloride and hence, the purity of the top draw-off should steadily decrease as the distillation proceeds. The results are summarized in Table IV. It will be noted that the activity decreased steadily as expected. It was also apparent that the difference in conversion between the first and last samples was nearly twice as great at 70°C. as at 80°C., i.e., 10.0 and 5.3%, respectively. Hence, 70°C. was adopted as the tem-

TABLE IV

Comparison of Conversions at 70 and 80°C.

Fraction no.	Conversion to polymer, %	
	At 70°C.[a]	At 80°C.[b]
1	42.8	38.2
2	41.9	35.6
3	39.3	35.1
4	36.9	35.3
5	35.0	33.4
6	32.8	32.9

[a] Concentration of benzoyl peroxide 1.25%, duration 2 hr.
[b] Concentration of benzoyl peroxide 0.625%, duration 1 hr.

perature of polymerization for the test. Under the final conditions of the test, a skilled technician after sufficient training is able to obtain results with absolute mean deviations of 0.5–1.0% which correspond to percentage deviations of 1.3–2.7%. Values which deviated more than 3% from the mean were usually rejected.

Effect of Various Compounds on the Rate of Polymerization of Vinyl Chloride

The effect of certain compounds, which may occur in commercial vinyl chloride, was studied. The results are summarized in Table V and Figures 3 and 4.

Addition of acetaldehyde up to a concentration of about 2% increased the rate of polymerization. Further additions decreased the rate. The average molecular weight of the polymer, however, decreased continuously

TABLE V

Effect of Various Compounds on the Rate of the Bulk Polymerization of Vinyl Chloride and on the Molecular Weight of the Polymer[a]

Compound added	Concn. of compd. added, %	Conversion to polymer, %	Change in conversion, %/ppm	Intrinsic viscosity, dl./g.[b]	Avg. molecular weight of polymer[c]
Acetaldehyde	0	38.0		0.66	22,000
	0.10	37.6			
	1.99	49.6	+0.00058	0.33	10,100
	3.86	44.8	+0.00018	0.20	5,760
	7.9[d]	40.7	+0.000035		
Crotonaldehyde	0	38.0		0.66	22,000
	0.0245	35.8			
	0.0485	33.0	−0.0103	0.60	19,800
	0.0942	30.7	−0.0078	0.61	20,100
Chloroprene	0	38.3		0.63	20,900
	0.0044	34.0		~0.5	~16,300
	0.0097	28.45	−0.10		
	0.0193	22.2		0.51	16,500
1,1-Dichloro-ethane	0	38.3			
	1.73	44.7	+0.00037		
	4.60	54.6	+0.00036		
trans-1,2-Di-chloroethylene	0	38.3		0.63	20,900
	0.87	39.2		0.54	17,600
	3.77	42.7	+0.00012		
Paraldehyde	0	38.0		0.66	22,000
	0.97	43.2	+0.00054	0.42	13,300
1,1,2-Trichloro-ethane	0	38.3			
	2.905	52.6	+0.0005		

[a] Bath temperature 70°C., concentration of benzoyl peroxide 1.25%, duration of polymerization 2 hr.

[b] Solvent tetrahydrofuran, temperature 25°C.

[c] Calculated from the formula of Talamini and Vidotto.[3]
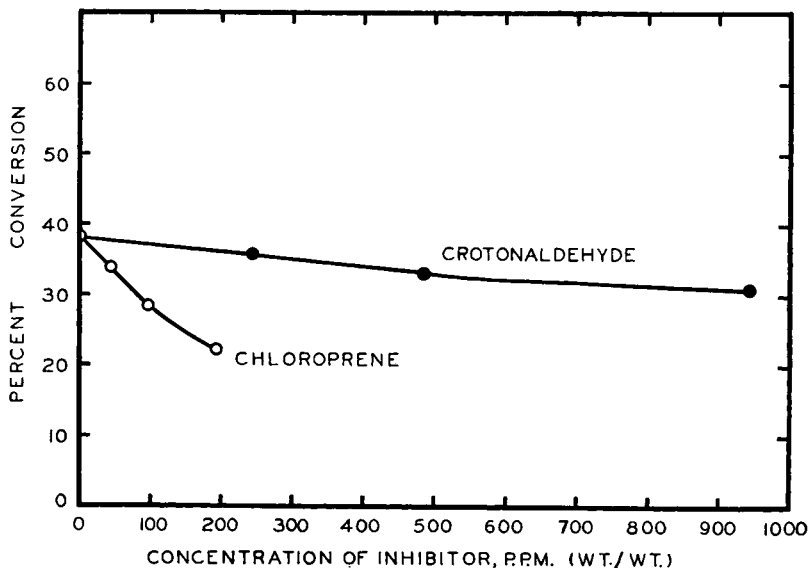
[d] Polymer yellow and crumbly.

Fig. 3. Effect of various concentrations of inhibitors on the percentage conversion of vinyl chloride.
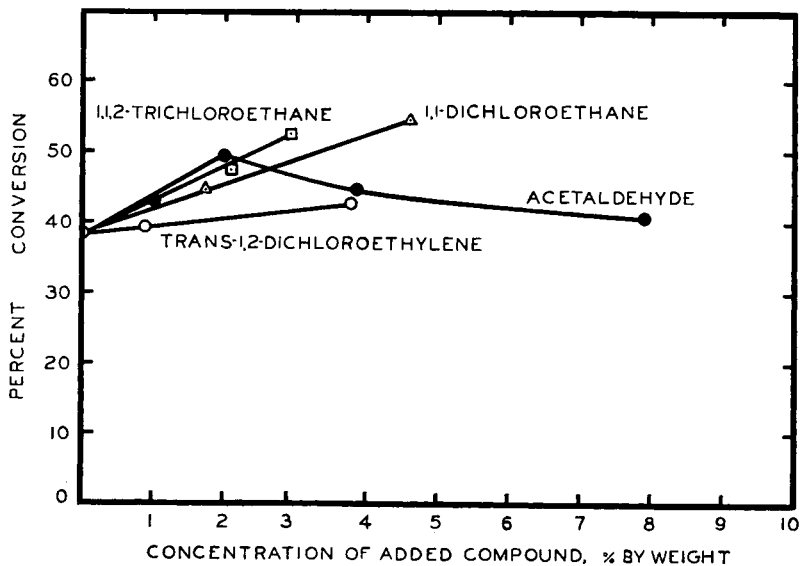

Fig. 4. Effect of various concentrations of added compounds on the percentage conversion of vinyl chloride.

as the concentration of acetaldehyde increased.   Paraldehyde accelerated the polymerization to the same extent as acetaldehyde, at least up to a concentration of 1%.

Crotonaldehyde and chloroprene were found to be strong inhibitors.

As in the previous investigations on vinyl acetate,[1,2] chloroprene was 11 to 12 times stronger than crotonaldehyde, on a molar basis. Also, as with acetaldehyde, the molecular weight of the polymer decreased with increase in the concentration of crotonaldehyde or chloroprene.

All the chlorinated hydrocarbons studied increased the rate of polymerization at concentrations from 0 to 5% and decreased the molecular weight of the polymer. 1,1,2-Trichloroethane was the strongest accelerator, followed by 1,1-dichloroethane and *trans*-1,2-dichloroethylene.

Experimental

The test is carried out in a stainless steel autoclave (Fisher Scientific Catalogue No. 13-555-100) containing a Pyrex glass liner (Fisher Scientific Catalogue No. 13-555-105). To ensure tightness, a second $1/8$-in. brass Hoke valve is connected to the existing valve. For good reproducibility the liners should be matched with regard to size and weight. The liners should weigh between 68 and 72 g. (without cover), must have an outside diameter of 1.905–1.935 in. (measured 1 in. from the bottom) and should have a height of 10.45–10.55 cm. Oversize liners usually give discolored polymer. The liner is cleaned by immersion first in acetone for 1–3 hr. to soften the old polymer and then in a saturated solution of potassium hydroxide in isopropanol for 8–24 hr. It is then rinsed at least 15–20 times with water, dried with acetone of good quality, and put in an oven at 110°C. for at least $1/2$ hr. It is removed from the oven 15–30 min. before using. The autoclave is cleaned in the following manner. The internal surface of the bottom part of the autoclave is wiped with a paper towel soaked with acetone to remove any adhering material. It is then rinsed three times with acetone and dried for 5–10 min. with hot air from a hair dryer. The rod is removed from the exit pipe, wiped with a towel soaked with acetone, rinsed with acetone, and dried with hot air. The outlet pipe is rinsed three times with acetone and put under vacuum for 10–15 min. The rod is then reinserted in the exit pipe. The composition gasket (Fisher Catalogue No. 13-555-115) is removed, rinsed with acetone, dried with a hair dryer, and replaced in position.

The glass liner is weighed on an analytical balance and 0.500 g. of benzoyl peroxide, which has been purified by reprecipitation from chloroform,[1] is added. About 18 ml. of purified mercury is filtered through a Dixie cup to remove any surface scum and is then carefully poured into the bottom part of the autoclave, making certain it does not splatter. (After each experiment the mercury is repurified by washing first with 20% nitric acid and then water, drying and distilling.)

The entire apparatus shown in Figure 1, including autoclave, liner, catalyst, stainless steel ring (cf. Fig. 2), and glass capillary tube is weighed to 0.05 g. on a Keller balance with a 10-kg. capacity. The total weight is about 3600 g. An alumina drying tube is attached to the liner by means of a tightly fitting rubber stopper and solid CO_2 is packed around the liner. After 10–15 min. the drying tube is removed and 52–60 ml. of cold (-30 to

−70°C.) vinyl chloride is quickly added from a Hoke stainless steel sampling cylinder (Catalogue No. 6 HD500 with an outage tube). The vinyl chloride is gently swirled for a few seconds to dissolve the benzoyl peroxide. The liner is wiped with a paper towel and quickly placed in the autoclave. The stainless steel ring (Fig. 2) is placed on top of the liner. (This forces the liner into the mercury when the top of the autoclave is screwed on.) The top of the autoclave is quickly screwed on and tightened gently with the appropriate wrenches. The autoclave is then evacuated as follows. The exit $1/8$ in. brass Hoke valve is connected to a water ejector, and the autoclave is evacuated to about 500 mm. Hg absolute for 5–10 sec. The Hoke valve is closed for 30–60 sec., and the autoclave is evacuated again to 500 mm. Hg absolute. Three such evacuations are sufficient. A 160-mm. length of glass capillary tube is attached to the exit Hoke valve and the entire assembly is placed on the Keller balance. The valves are cracked open and the vinyl chloride allowed to evaporate slowly until 40.0 ± 0.1 g. of monomer is left in the autoclave. The valves are quickly closed and the final weight of the monomer recorded. The bottom part of the autoclave (up to the expanded section) is immersed in a water bath at room temperature for 2 min. and then in a water bath maintained at 70.0 ± 0.05° C. with a Bronwill constant temperature circulator for exactly 120 min. The autoclave is stationary throughout the polymerization, and its top surface is horizontal. The autoclave is then placed in a brine bath (−12° C.) for about 300 sec., followed by a Dry Ice–isopropanol bath for an additional 300 sec. The valves are then slowly opened with a piece of filter paper on the outlet pipe to prevent rapid entry of air which may cause the mercury to be blown into the polymer. With the valves open, the autoclave is placed in a water bath at room temperature for 30 min. to evaporate most of the unreacted monomer. The liner is then removed from the autoclave, and wiped with a towel to remove any adhering mercury. It is placed in a water bath at 63 ± 2°C. and the residual monomer evaporated for 1 hr., under reduced pressure (10–15 mm. Hg absolute).

After cooling, the liner and its contents are weighed on an analytical balance. From this gross weight are subtracted the tare weight of the liner and 0.500 g. for the catalyst to give the weight of polymer. The weight of polymer divided by the weight of monomer (i.e. 40.0 ± 0.1 g.), and multiplied by 100 gives the percentage conversion. The polymer obtained from good grade monomer is white in color. The total time required to carry out the test is about 5 hr. However, the minimum length of time needed to evaporate all the unreacted monomer was not established and hence, some reduction in the total time required for the test may be possible.

References

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Résumé

Un test de l'activité de polymérisation a été développé afin d'évaluer la pureté du chlorure de vinyle commercial.   Quarante grammes de chlorure de vinyle sont chauffés avec 0.5 gr. de peroxyde de benzoyle pendant deux heures à 70°C dans un manchon de verre dans une autoclave en acier inoxydable, et le poids du polymère formé est déterminé. Les effets de l'agent de transfert de chaleur dans l'autoclave, du temps, de l'oxygène, de l'agitation limitée, de la concentration en catalyseur et de la température sur le pourcentage de conversion de monomère en polymère ont été déterminés.   L'effet de l'acétaldéhyde, du crotonaldéhyde, du chloroprène, du 1,1-dichloroéthane, du *trans*-1,2-dichloroéthylène, du paraldéhyde et du 1,1,2-trichloroéthane sur la conversion ainsi que le poids moléculaire du polymère sont dècrits.

Zusammenfassung

Zur Bestimmung der Reinheit von handelsüblichem Vinylchlorid wurde ein Polymerisationsaktivitätstest entwickelt.   Vierzig Gramm Vinylchlorid werden mit 0,500 g. Benzoylperoxyd während 2 Stunden in einem Glasgefäss in einem Autoklaven aus rostfreiem Stahl auf 70°C. erhitzt und das Gewicht des gebildeten Polymeren bestimmt. Der Einfluss des Wärmeübertragungsmittels im Autoklaven, der Dauer, der beschränkten Bewegung, Katalysatorkonzentration und Temperatur auf die prozentuelle Umwandlung von Monomerem in Polymeres wurde bestimmt.   Der Einfluss von Acetaldehyd, Krotonaldehyd, Chloropren, 1,1-Dichloräthan, *trans*-1,2-Dichloräthylen, Paraldehyd und 1,1,2-Trichloräthyn auf Umsatz und Molekulargewicht des Polymeren wird beschrieben.