

## Vapor Phase Polymerization of Vinyl Chloride

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### Synopsis

A study of the polymerization of vinyl chloride was made at conditions under which the monomer exists in the gas phase. In the presence of a bed of poly(vinyl chloride) particles, free-flowing product was obtained. By using free-radical initiators, such as dialkylperoxy dicarbonates or acetylcyclohexane sulfonyl peroxide, high initiator productivities were obtained in reaction periods of 1.5 to 3 hr. Although some modifiers, such as ethyl bromomalonate and bromoform, were demonstrated to lower molecular weight, satisfactory molecular weight modification was accomplished by adjusting polymerization temperature. Several peroxy compounds of different reactivity were studied. Hydrocarbon additives improve the polymerization rate. It is believed that the hydrocarbon and initiator are absorbed on the PVC particle surface and allow the monomer concentration to be increased at the polymerization locus. PVC particles of small size may be prepared in a liquid bulk polymerization for use as seed polymer for the vapor phase process. This provides a seed of high porosity which enables one to prepare a vapor phase product with suitable plasticizer absorption. The physical properties of products prepared by the vapor phase process were evaluated in a rigid formulation.

### INTRODUCTION

Historically, poly(vinyl chloride) resins have been produced in four types of polymerization systems: emulsion, aqueous suspension, solution, and bulk. In the U.S., about 80% of the PVC is made in aqueous suspension systems and about 15% in emulsion systems.<sup>1</sup> Bulk polymerization of vinyl chloride has begun recently to gain consideration for new capacity.<sup>2,3</sup>

This paper is concerned with a novel variation of bulk polymerization wherein the vinyl chloride monomer is in the vapor phase. High rates were accomplished by the use of highly reactive peroxy compounds and the presence of hydrocarbon additives.

### EXPERIMENTAL

#### Polymer Preparation

The vapor phase polymerizations of vinyl chloride were conducted in a stainless steel reactor of 1-liter capacity. The reactor was provided with an internal cooling coil and an anchor-type stirrer for agitation of the dry poly(vinyl chloride) bed (Fig. 1). The reactor was flushed with nitrogen gas, and 100 g of a degassed commercial, general purpose-grade PVC powder was

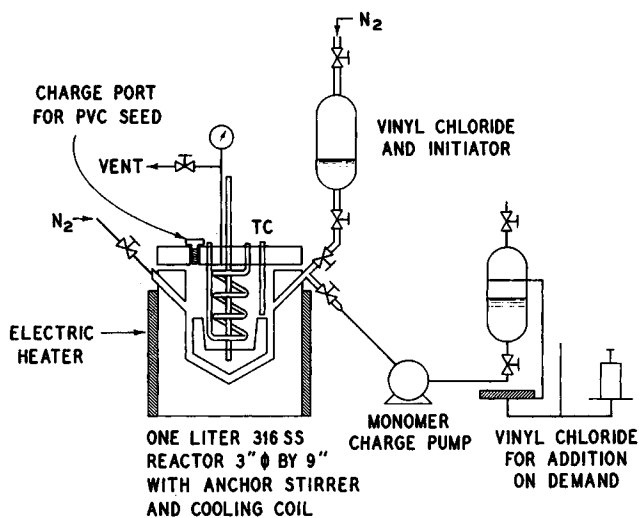


Fig. 1. Apparatus for vapor phase polymerization of vinyl chloride.

charged to the reactor as seed. Additives were charged by syringe or pipet through the charge port with resin bed agitation. The reactor was then closed and flushed three times with vinyl chloride vapor at 35 psig. With pressure on the reactor and with agitation, the reactor was heated to operating temperature.

Melted initiator was transferred to a cooled charge cylinder using a cooled 0.2-ml pipet. The charge cylinder was closed, immersed in ice water, and flushed with vinyl chloride vapor. The desired amount of vinyl chloride was then distilled from a storage cylinder at room temperature and condensed in the charge cylinder. The contents of the charge cylinder were pressured into the heated reactor with nitrogen gas. Operating pressure was maintained for the desired polymerization time by pumping vinyl chloride into the reactor on demand.

At the end of the reaction period, the polymerization was terminated by venting monomer; no shortstop was employed. The polymer was removed

TABLE I  
Recipe for Rigid PVC Formulation

	Parts by weight
Poly(vinyl chloride)	90
Blendex 401 <sup>a</sup>	10
Advastab T-360 <sup>b</sup>	2
Advawets DBTDL <sup>b</sup>	1
Advawax 280 <sup>c</sup>	0.5
Advawax 140 <sup>c</sup>	0.5

<sup>a</sup> A commercial acrylonitrile-butadiene-styrene terpolymer.

<sup>b</sup> Commercial stabilizers.

<sup>c</sup> Commercial processing aids.

from the reactor and dried in a vacuum oven at 150°F for 3 hr using a nitrogen gas purge.

### Compounding and Evaluation

The experimental polymers for evaluation were compounded in a common recipe (Table I) and compression molded at 370°F.

## RESULTS AND DISCUSSION

### Polymerization Variables

When a vapor phase polymerization of vinyl chloride was conducted at 140°F employing diisopropyl peroxydicarbonate (IPP) as initiator, a productivity of 705 g of PVC per gram of initiator was obtained in 1.5 hr.

TABLE II  
Effect of Hydrocarbons on Vapor Phase Polymerization of Vinyl Chloride

Hydrocarbon <sup>a</sup>	Productivity, <sup>b</sup> g/g IPP <sup>c</sup>
None	705
<i>n</i> -Pentane	1140
Neopentane	1150
Cyclopentane	1850
2,3-Dimethylbutane	1605
Methylcyclopentane	1480
Cyclohexane	1610

<sup>a</sup> Amount of hydrocarbon added was 6.6 ml.

<sup>b</sup> Conditions: 140°F, 115 psig using 0.07 g IPP and 100 g PVC seed for 1.5 hr.

<sup>c</sup> Laboratory preparation of IPP.

TABLE III  
Effect of Temperature and Pressure on Vapor Phase  
Polymerization of Vinyl Chloride

Temperature, °F	Pressure, psig	Productivity, <sup>a</sup> g/g IPP
120	82	585
125	90	770
130	102	923
135	110	1576
140	115	1610
145	125	1885
150	130	1904

<sup>a</sup> Conditions: 100 g PVC seed in a 1-liter reactor for 1.5 hr; 6.6 ml cyclohexane; 0.07 g IPP.

Initiator productivity or yield was found to be enhanced by the addition of a small amount of hydrocarbon to the system. In many cases, rates of polymerization were doubled or better for this reaction period. These data are summarized in Table II.

TABLE IV  
Effect of Time on Vapor Phase Polymerization

Time, hr	Temp., °F	Pressure, psig	Productivity,* g/g IPP	Rate, g/g IPP/hr
1.5	120	82	585	390
3	120	82	1388	462
6	120	82	2015	336
1.5	130	102	923	615
3	130	102	1525	508
6	130	102	3070	512
1.5	140	115	1610	1073
3	140	115	2110	704
6	140	115	2224	371

\* Conditions: 100 g PVC seed, 6.6 ml cyclohexane, 0.07 g IPP.

Although the precise reason for this increase in rate is not known, it is believed to be related to a better monomer-to-initiator contact on the surface of the resin particles.

To more fully characterize this system, polymerizations were initiated at temperatures in the range from 120° to 150°F (Table III).

In all cases, vinyl chloride pressure (reactor pressure) was maintained at 5 to 10 psig below that pressure at which vinyl chloride condenses. An increase in yield based on initiator with an increase in temperature was found throughout this range.

Table IV lists data at three different temperatures for three different reaction periods. Although initiator productivity increased with time, rate data indicate an optimum initiator efficiency is reached at a different time

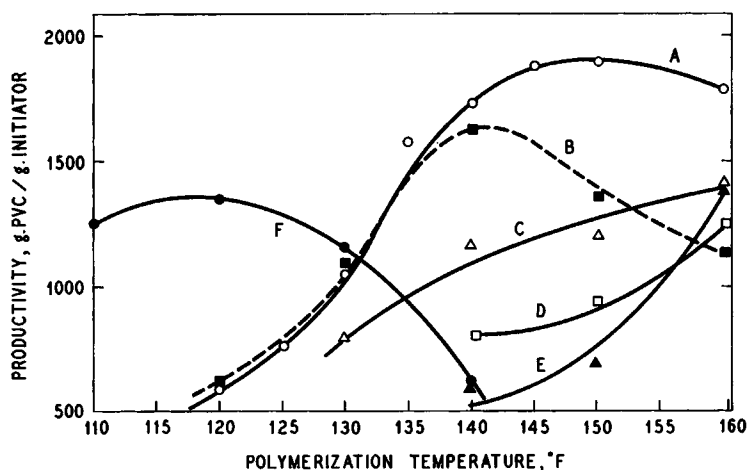


Fig. 2. Effect of temperature on productivity for various free-radical initiators for 1.5 hr reactor time: (A) diisopropyl peroxydicarbonate; (B) acetylcyclohexane sulfonyl peroxide; (C) di(*sec*-butyl) peroxydicarbonate; (D) dicyclohexyl peroxydicarbonate; (E) di(2-ethylhexyl) peroxydicarbonate; (F) isobutyryl peroxide.

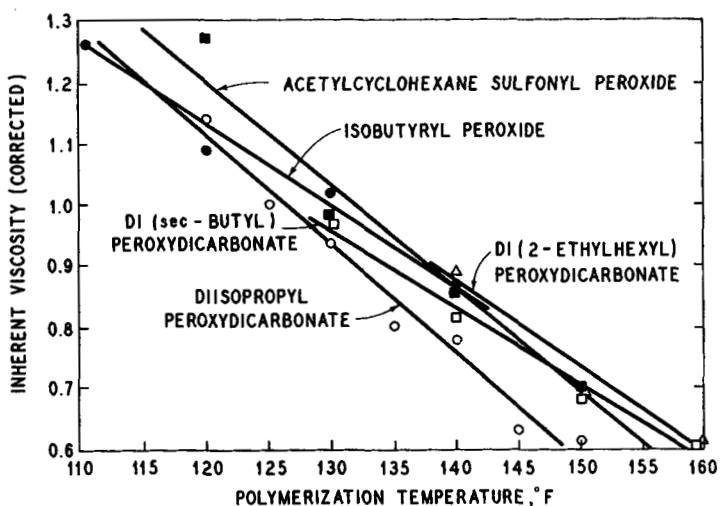


Fig. 3. Effect of temperature on inherent viscosity of vapor phase PVC made with various initiators.

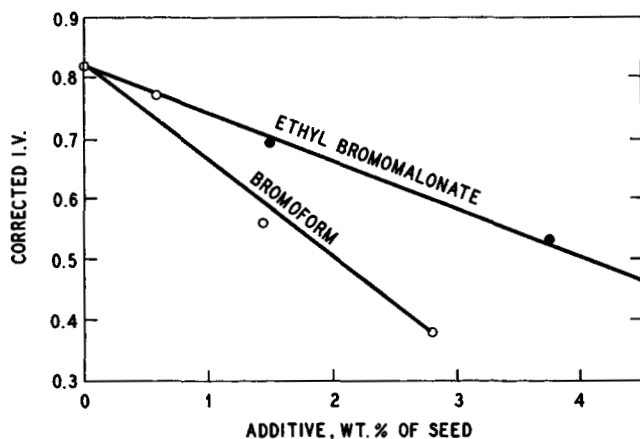


Fig. 4. Effect of additives on inherent viscosity of vapor phase PVC (140°F).

for each temperature. The highest initiator productivity of 3070 g PVC per g initiator was obtained at 130°F in 6 hr.

The differences in productivity versus initiator structure over a temperature range of 110° to 160°F are illustrated in Figure 2. The initiators in Figure 2 were obtained, in part, through the courtesy of Lucidol Division of Wallace and Tiernan, Inc., and are identified as: A, Luperox IPP; B, Luperox 228; C, Lupersol 225; D, Luperox R229; E, Lupersol 223; and F, Lupersol 227. Diisopropyl peroxydicarbonate (A) was the most efficient within this temperature range, followed closely by acetylcyclohexane sulfonyl peroxide (B). The very reactive isobutyryl peroxide (F) was the

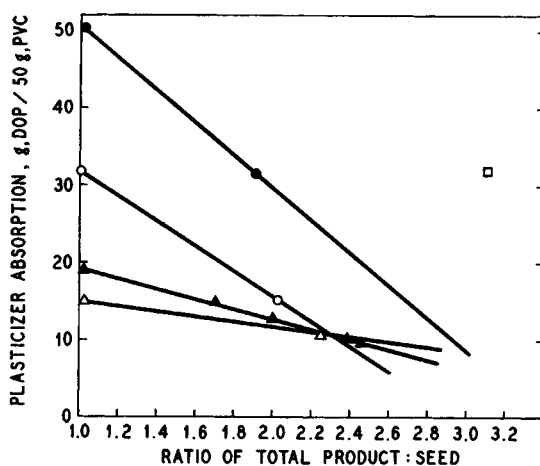


Fig. 5. Absorption of dioctyl phthalate (DOP) in vapor phase PVC: (●) seed: 50 g/50 g; (○) seed: 32 g/50 g; (▲) seed: 19 g/50 g; (△) seed: 15 g/50 g.

most efficient at 120°F and, as shown in Figure 2, would be very efficient for the preparation of high molecular weight product.

As in suspension and emulsion polymerization systems, the molecular weight of poly(vinyl chloride) is dependent on the polymerization temperature (Fig. 3). Although there is some variation among the different types of initiators, a linear relationship appears to exist over this temperature range for inherent viscosity. The inherent viscosities were corrected for the presence of seed polymer. Variations in viscosity from initiator to initiator

TABLE V  
Properties of Vapor Phase PVC

Initiator type <sup>a</sup>	IPP	IPP	ASP	Resin <sup>b</sup>
Polymerization Data				
Cyclohexane, ml	6.6	—	—	—
Temperature, °F	140	140	140	—
Pressure, psig	115	115	115	—
Time, hr	3.0	3.0	1.5	—
Productivity, g PVC/g initiator	2250	1800	1847	—
Inherent viscosity	0.80	0.86	0.78	0.82
Properties in Rigid Formulation				
Density, g/cc	1.338	1.346	1.347	1.340
Flexural modulus, psi × 10 <sup>-3</sup>	366	336	384	377
Tensile yield, psi	7337	7275	7550	7200
Elongation, %	136	135	136	99
Izod impact, ft-lb/in. notch	2.88	2.39	1.81	2.77
Hardness, Shore D	82	83	82	80

<sup>a</sup> IPP Diisopropyl peroxydicarbonate; ASP = acetylcyclohexane sulfonyl peroxide.

<sup>b</sup> A commercial general-purpose resin.

at a given temperature are probably due in part to this correction as well as temperature control in this small reactor for a heterogeneous mixture.

Active bromine compounds also functioned as molecular weight modifiers. In Figure 4, the effect of bromoform and ethyl bromomalonate on inherent viscosity at 140°F polymerization temperature is shown. By the use of these bromine compounds, it was possible to prepare polymers of lower molecular weight at the temperature when the initiator is most efficient.

Invariably, dioctyl phthalate (DOP) absorption decreased with reactor residence time for a given seed polymer. In Figure 5, plasticizer absorption is plotted against the ratio of total product weight to seed weight. Four different seed polymers having plasticizer absorptions of 15, 19, 32, and 50 g DOP/50 g PVC (see ordinate at ratio = 1.0, Fig. 5) were chosen to illustrate this effect. However, the single point at a 3.1 ratio of 32.0 g DOP/50 g PVC indicates that a polymer of high DOP absorption can be made in this gas phase system. The seed for this product was made in the reactor in a liquid bulk polymerization prior to the establishment of vapor phase conditions.

### Polymer Properties

Physical properties of typical vapor phase products were tested as shown in Table V. These data demonstrate that poly(vinyl chlorides) made in this vapor phase system possess properties similar to those for a commercial suspension PVC.

### References

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