

# Synthesis of Vinyl Phenyl Acetate and an Evaluation of Vinyl Chloride/Vinyl Phenyl Acetate Copolymers

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## SYNOPSIS

The synthesis of vinyl phenyl acetate, by an ester interchange reaction between phenyl acetic acid and vinyl acetate and utilizing a catalyst, is described. Copolymerization with vinyl chloride, in a suspension system and using a peroxide catalyst, is described on a laboratory and pilot plant scale. Monomer/copolymer compositions, for an initial charge consisting of vinyl chloride/vinyl phenyl acetate (80/20 by weight) are presented over a range of conversions, as an indication of reactivity ratios. Discs, molded from unstabilized copolymers, show very good clarity and color stability, which improve with increased comonomer loading. Some retention of unpolymerized vinyl phenyl acetate monomer occurred, and some increase in softening points resulted following two reprecipitations from acetone into excess methanol. Compound from a 96/4 vinyl chloride/vinyl phenyl acetate copolymer has better color stability than does an equivalent vinyl chloride/vinylidene chloride copolymer compound. The enhanced color and heat stability of the copolymers is attributed to the aromatic character of the comonomer vinyl phenyl acetate.

## INTRODUCTION

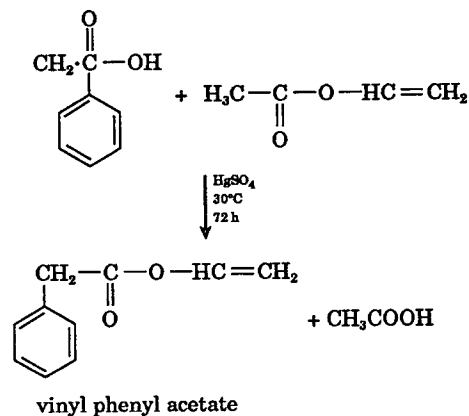
As part of a research project, concerned with the synthesis of copolymers of vinyl chloride with enhanced heat stability, the possibility of utilizing a suitable aromatic vinyl monomer was considered. Following a literature search, and bearing in mind economic factors, e.g., cost of starting materials, it was concluded that the synthesis of the vinyl derivative of phenyl acetic acid and then copolymerization with vinyl chloride should be investigated.

## EXPERIMENTAL

### Preparation of Vinyl Phenyl Acetate

A preliminary search of the literature<sup>1-3</sup> revealed that vinyl phenyl acetate had been prepared by a high-pressure reaction between acetylene and phenyl acetic acid. The method adopted in this work

utilized the interchange reaction of vinyl acetate with phenyl acetic acid, in the presence of mercuric sulfate as catalyst. Copper octoate was used as a polymerization inhibitor. The reaction can be represented as follows:



The mild reaction conditions and low yields of by-products lead to a high yield of monomer of greater

purity than that synthesized by the acetylene reaction.

### Materials

Phenyl acetic acid	1 mol
Vinyl acetate	6 mol
Mercuric acetate	2% by wt of acid
Concentrated H <sub>2</sub> SO <sub>4</sub>	0.5% by wt of acid
Copper octoate	0.1 g per mol of acid

### Procedure

Phenyl acetic acid was weighed into a two-necked flask and covered with the correct amount of freshly distilled vinyl acetate. Copper octoate, followed by mercuric acetate, were added and the concentrated sulfuric acid added dropwise with constant shaking. The reaction mixture was then allowed to stand in an oven at 30°C for 72 h. At the end of this time, sodium acetate (3% by weight of phenyl acetic acid used) was added with shaking.

Excess vinyl acetate, followed by acetic acid, were removed by distillation under reduced pressure on a water bath. A fraction boiling at 82–86°C/3–4 mmHg was then collected. Redistillation through a 9 in. column packed with Fenske helices isolated pure monomer. The following data refer to a typical preparation:

Yield of redistilled monomer	approximately 75% theory
Ester assay:	95% +
Boiling point:	85–86°C/3.9 mmHg
$n_D^{20}$ :	1.5120
Density (15°C):	1.047 g cm <sup>-3</sup>

The synthesis was repeated a number of times to provide sufficient monomer for tube scale and 15 gal scale copolymerizations.

### Copolymerization with Vinyl Chloride

Because of limitations on the amount of monomer synthesized, most of the copolymerization work with vinyl chloride was done on glass tube scale (total available volume ca. 250 mL). The 15 gal scale polymerization was restricted to a single batch of 96/4 vinyl chloride/vinyl phenyl acetate copolymer.

### Tube Scale

Initial polymerizations were carried out using a Geon 425 dispersion system, phase ratio, and initiator

loading. Very coarse polymer agglomerations were obtained with the Geon 425 gelatine loading, and treble the normal concentration was required to give a good polymer dispersion. The final formulation was the following:

	Parts by weight
Vinyl chloride	Various 100.0
Vinyl phenyl acetate	Various
Gelatine	0.264
Sodium bicarbonate	0.375
Caprylyl peroxide	0.325
Distilled water	280.0

Polymerization conditions—16.5 h at 62°C with end-over-end rotation—gave high conversion of a wide range of monomer mixtures.

### Copolymer Series

Two series of copolymerizations were carried out with 0, 5, 7.5, 10, 15, and 20% vinyl phenyl acetate (by weight, based on total monomer). The normal Geon 425 gelatine loading was used for the first series, and 3× the normal gelatine, for the second series. Polymers were purified by several washings with ethyl alcohol and then dried to constant weight at 40°C under vacuum.

Chlorine content, specific viscosity, and softening point were determined on each polymer as isolated by the procedure described. Polymers were then Soxhlet extracted for 24 h with ethanol, and the chlorine content was redetermined on extracted material. Data relating to this series are given in Table I. The softening-point determination is performed by the National Bureau of Standards method. This consists of measuring the sag of a cantilever beam in 1 h at constant temperature. The procedure is repeated at 5.6°C intervals. The temperature at which the beam sags a total of 0.1 in. (2.54 mm) is taken as the softening point. Wiley<sup>4</sup> quotes figures obtained by his method for the glass transition temperature ( $T_g$ ) of a number of commercial plastics, which indicates close correlation is attainable (Table II).

To obtain some insight into reactivity ratios, a vinyl chloride/vinyl phenyl acetate (80/20 by weight) polymerization was performed. Monomer composition versus copolymer composition over a range of conversions were determined (Fig. 1).

Vinyl phenyl acetate has a characteristic odor

**Table I Tube-Scale Copolymer Series**

Recipe	Wt % VCl	Wt % VPA	Conversion	Wt % Non-Cl <sub>2</sub> Material	* $\eta_{sp}$	Softening Point (°C)	% Cl <sub>2</sub> Extract	Wt % Non-Cl <sub>2</sub> Material Extracted Polymer
Normal gelatine loading	100	0	96	2.5	0.47	78.6	3.7	2.5
	95	5	95	6.2	0.45	73.2	4.7	6.0
	92.5	7.5	95	8.6	0.40	69.8	4.0	10.2
	90	10	96	11.7	0.39	65.6	5.0	13.8
	85	15	91	18.5	0.30	55.5	5.0	
	80	20	89	25.0	0.23	44.8	6.2	
3 × normal gelatine	100	0	98	1.0	0.47	78	2.3	1.0
	95	5	95	6.2	0.47	73	2.1	6.2
	92.5	7.5	92	9.5	0.43	70	4.9	10.2
	90	10	94	11.8	0.37	66.7	4.1	10.9
	85	15	91	17.1	0.34	56	5.2	16.2
	80	20	92	22.4	0.29	51	2.2	23.5

Softening point of Geon 425 = 62.9°C (mean), standard deviation = 0.28°C. VCl = vinyl chloride; VPA = vinyl phenyl acetate; and \* $\eta_{sp}$  = 0.5% solution in cyclohexanone at 25°C.

that was noticeable in all of the “dried” copolymers. It was thought that the copolymers contained residual amounts of unpolymerized vinyl phenyl acetate. To eliminate the possible presence of the monomer, copolymers were reprecipitated twice from acetone by pouring into excess methanol. Small increases in softening points occurred, indicating that residual monomer could lower both these and  $T_g$  values. Free monomer is obviously present, but it appears, generally, to be a relatively small proportion of the amount charged.

Composite moldings made from Geon 425, a copolymer of vinyl chloride and vinyl acetate (80/20), and each copolymer of the series were examined for color and clarity. A striking and continuous improvement of color stability was observed ascending in the copolymer series. A clear, nearly water-white molding was obtained for the copolymer made from the 85/15 vinyl chloride/vinyl phenyl acetate polymerization.

**Table II Copolymer Properties Following Two Acetone Reprecipitations**

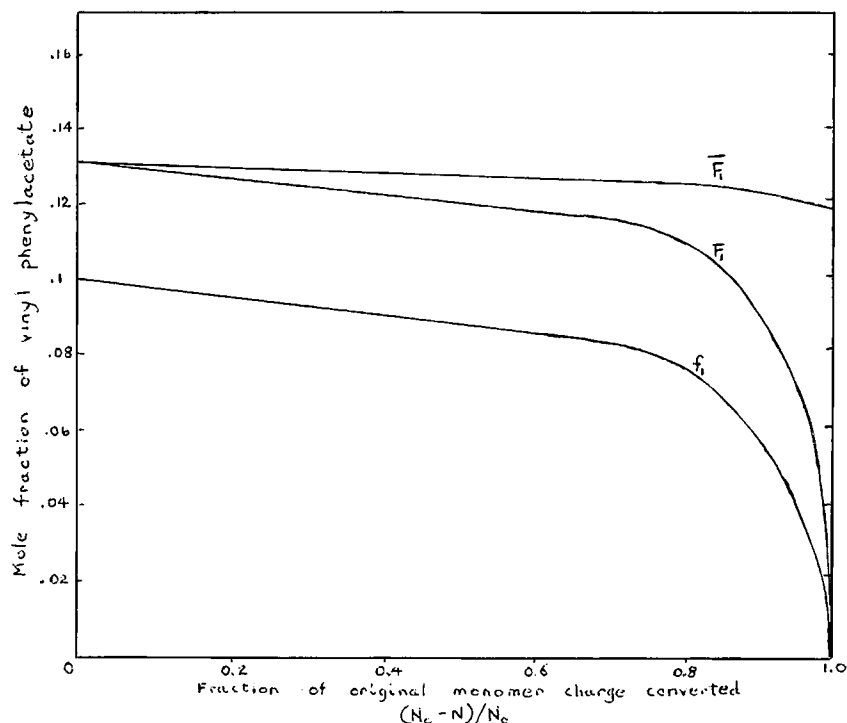
Wt % VCl	Wt % VPA	Wt % Non-Cl <sub>2</sub> Material	$\eta_{sp}$	Softening Point (°C)
100	0	0.7	0.48	79
95	5	5.6	0.48	75
92.5	7.5	8.4	0.45	72
90	10	10.7	0.40	68
85	15	16.4	0.37	59
80	20	20.6	0.32	54

Composite moldings were also made from copolymers that had been extracted with ethyl alcohol. Compared with moldings of unextracted polymers, there was a slight deterioration in the color stability of high vinyl phenyl acetate copolymers, but steady improvement still occurred with increasing vinyl phenyl acetate content. The color and clarity of all moldings were significantly better than that of the control Geon 425 polymer, which was reddish-brown under the molding conditions chosen. There was no deterioration in the color stability of a copolymer after reprecipitation from acetone solution.

#### 87.5/12.5 Vinyl Chloride/Vinyl Phenyl Acetate Copolymer

It was estimated, from the data in Table I, that a copolymer made from 87.5/12.5 vinyl chloride/vinyl phenyl acetate monomer mixture would have approximately the same softening point as does Geon 425. About 400 g of the copolymer was obtained by blending the products of a number of tube-scale polymerizations. Polymer and compound properties were compared with those of Geon 425 (see Table III):

Compound formulation:	100/1/1/1 Polymer/white lead paste/ calcium stearate/ lead stearate
Rolls temperatures (Francis Shaw):	160/140°C
Milling time:	5 min



**Figure 1** Polymer and monomer compositions as functions of conversion for vinyl chloride/vinyl phenyl acetate (0.9/0.1 mol fraction) charge.  $F_1$  is the mol fraction of vinyl phenyl acetate in the polymer being formed at a point where feed composition has moved to  $f_1$ .  $\bar{F}_1$  is the average composition of all the polymer formed up to that point.

Comparing hot-melt plasticity on the Macklow-Smith Index it appears that Geon 425 has somewhat better flow properties than does a vinyl phenyl acetate copolymer, which has the same softening point. Very good color and clarity were again found for the vinyl phenyl acetate copolymer component of a composite disc with Geon 425.

**Table III Copolymer and Compound Properties**

Polymer	VC/VPA Copolymer (87.5/12.5)	Geon 425
$\eta_{sp}$	0.38	0.35
Non-Cl <sub>2</sub> -containing material (%)	12.7	18.9
Congo-Red heat stability (min)	13	5-10
Compound		
Congo-Red heat stability (min)	27	32
Softening point (°C)	63	64
Macklow-Smith Flow (psig)		
145°C	3140	2800
155°C	2360	2100
165°C	1940	1600

### 15 Gal Scale Polymerization 96/4 Vinyl Chloride/Vinyl Phenyl Acetate Copolymer

One 15 gal scale batch of copolymer was prepared from 96/4 vinyl chloride/vinyl phenyl acetate (Ref. 52011/148) by a modified Geon 202 process and compared with a 96/4 vinyl chloride/vinylidene chloride copolymer (52011/19) produced under the same conditions.

General physical properties such as specific viscosity, softening point, and Macklow-Smith flow

**Table IV Color Stability of Copolymer Compound and Geon 202 Compound**

Time of Milling (min)	% White Light Reflected		
	Geon 202	52011/19 CIV <sub>2</sub> Copolymer	52011/148 VPA Copolymer
5	50	—	62
10	48.5	53.4	57.8
15	45.0	50.4	53.0
20	42.5	48.7	50.0
25	40.0	47	46.3
30	38.5	44.8	44.0

**Table V Softening Points and Transition Temperatures of Selected Polymers**

Polymer	Softening Point (°C)	Transition Temperature ( $T_g$ ) (°C)
Methacrylate x-6	127	124
Cellulose nitrate F-2	68	72
Cellulose acetate C-23	57	57
Vinyl copolymer L-9	54	53
Methacrylate K-24	61	60

Data from H. R. Fleck, *Plastics, Scientific and Technological*, 2nd Edition, The English Universities Press Ltd., London, 1945.

were approximately the same for the two polymers, but there were noticeable differences in color stability. The experimental vinyl phenyl acetate copolymer, molded in a composite disc with Geon 202, showed much improved color and clarity compared with the control. 52011/19 showed only a small improvement. The stability of the compound was estimated as follows:

A comparison was made between the two polymers described above and Geon 202, a copolymer of vinyl chloride and vinylidene chloride (95/5). Each was compounded in the formulation 100/6/0.25, polymer/white lead paste/lead stearate, and milled on the 18 in. Roggermann 2 roll mill, with roll temperatures of 160–140°C. Strips of compound cut from the mill batch at 5 min intervals up to 30 min were press-polished, and reflectances of white light were measured with an EEL Electrometer (see Table IV).

The color stability of the VPA copolymer is therefore somewhat better than that of an equivalent  $VCl_2$  copolymer for milling times on compounds up to 20 min. Because of the difficulty in preparing sizable quantities of comonomer, the color stabilities of polymers containing higher proportions of VPA were not evaluated by this test.

## DISCUSSION

The experimental results demonstrate that copolymers of vinyl chloride and vinyl phenyl acetate have

enhanced color stability, in the absence of an external stabilizer or other compound ingredients. Additionally, the limited work on the heat and color stability of the copolymers, in compound formulations, indicate advantages over vinyl chloride/vinylidene chloride copolymer with the same external stabilizers.

It is considered possible that the inherent stability of aromatic structures, particularly at elevated temperatures, may enhance the thermal stability of vinyl chloride when incorporated in the polymer chain. This may have the effect of inhibiting the onset of hydrogen chloride evolution, which can result in pure poly(vinyl chloride), the consequential formation of double bonds, and the resulting appearance of reddish-brown color.

Some residual unpolymerized vinyl phenyl acetate remains after polymerization, and this does tend to depress softening points. This is indicated by the results obtained when the test was repeated on copolymers reprecipitated twice from acetone, as shown in Table II.

From the limited work on one copolymerization (VC/VPA, 80/20 by weight), reactivity ratios appear favorable. Figure 1 illustrates copolymer and monomer compositions during the polymerization cycle.

From an economic viewpoint, the raw material costs, for the principal materials in the synthesis of vinyl phenyl acetate, viz. phenyl acetic acid and vinyl acetate, are \$23/kg and \$8/kg are modest. For significantly larger quantities, unit costs would be lower. It is considered that further development, of vinyl phenyl acetate copolymers could be advantageous, particularly for applications where color stability is of prime importance.

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