

Cross-Linking in the Polymerization of Vinyl Benzoate and Related Compounds*

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In the course of a study of vinyl ester polymerizations and copolymerizations it was observed that vinyl benzoate-vinyl acetate mass copolymers formed swollen gels in typical solvents for polyvinyl esters such as acetone, ethyl acetate, dioxane, chloroform, and carbon tetrachloride. Soluble vinyl benzoate-vinyl acetate copolymers were readily prepared by conducting the copolymerizations in dioxane or benzene solutions.

It was at first suspected that the cross-linking might be the result of impurities in the vinyl benzoate used. This sample had been prepared from acetylene and benzoic acid by a vapor phase reaction over zinc acetate supported on activated carbon and had been carefully fractionated. Following the observation of copolymer gelation the vinyl benzoate was re-fractionated under reduced pressure using a $1\frac{1}{2}$ " $\times$ 48" glass column packed with glass helices. No significant variation in boiling point (86°C./12 mm.) was observed, so fractionation was based on a minor variation in refractive index during distillation. Each of seven fractions was used in producing mass copolymers of 40% vinyl benzoate-60% vinyl acetate. All copolymers were cross-linked and no variation in tendency to cross-link was noted among the samples.

In addition, vinyl benzoate was prepared by acidolysis of vinyl acetate with benzoic acid in the presence of mercuric acetate.¹ The refractionated product was copolymerized in mass with vinyl acetate and gelled products were also obtained. The fact that vinyl benzoate prepared by two independent routes yielded gelled copolymers serves to substantiate the belief that this compound is bifunctional in polymerization.

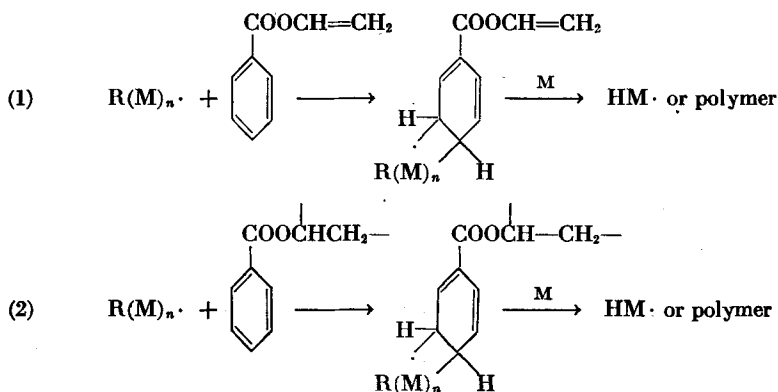
Mass polymerization of vinyl benzoate produces a cross-linked, hard, brittle, and crystal-clear resin. Furthermore, emulsion terpolymers of vinyl benzoate, vinyl acetate, and butyl acrylate of widely varying composition were without exception cross-linked.

Emulsion copolymerization of vinyl acetate with vinyl *p*-methoxybenzoate, vinyl *p*-chlorobenzoate, vinyl *o*-chlorobenzoate, vinyl *m*-toluate, vinyl *p*-toluate, and vinyl *p*-phenylbenzoate also produced cross-linked products. These copolymers were compression-moldable, in spite of poly-

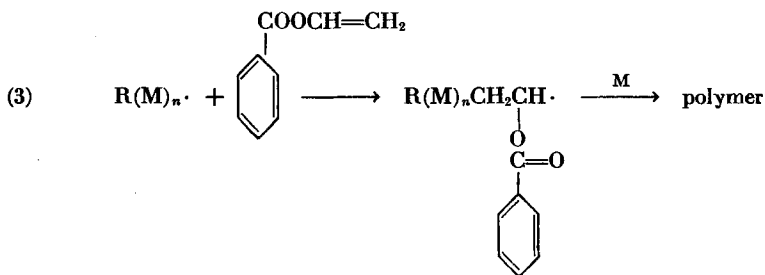
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mer gelation. These vinyl benzoate derivatives were prepared by acid exchange between vinyl acetate and the corresponding acids in the presence of mercuric acetate.

All of these facts strongly support the belief that vinyl benzoate and related compounds possess an activated ring double bond which may enter into copolymerization in a normal fashion or terminate a growing free radical in a manner similar to that proposed for benzoquinone and *m*-dinitrobenzene by Price.² On this basis, addition of the free radical in the *para* position (or in the *ortho*- or *meta*- position if the *para*-position is blocked) may occur to yield a resonance-stabilized structure. Presumably, free radical addition to the ring could occur with either vinyl benzoate monomer or interpolymerized vinyl benzoate:



These reactions would be expected to be equally probable and should occur at approximately the same rate. Coupled with the normal addition of the vinyl monomer to a growing free radical:



a network structure may be readily obtained. The nuclear reactivity of vinyl benzoate would be expected to be reflected in the r_1 and r_2 reactivity ratios in copolymerization. These values should be significantly different from those of vinyl esters lacking ring activity. This effect is indeed found in copolymerization of vinyl esters with acrylonitrile.³ Acrylonitrile is twelve times as reactive with a vinyl 2-ethylhexoate free radical as vinyl 2-ethylhexoate and only five times as reactive with a vinyl benzoate free radical as vinyl benzoate. From these data a chain transfer constant of

0.14 may be calculated for the ratio of the reactivity of the benzene nucleus of vinyl benzoate and interpolymerized vinyl benzoate with an acrylonitrile free radical to the reactivity of acrylonitrile with an acrylonitrile free radical.

In addition to the mechanism of cross-linking based on free radical addition to the benzoate nucleus as proposed above, it is possible that cross-linking may arise from replacement of the tertiary hydrogen α to the ester group in the polymeric chain. To establish the correct mechanism it is planned at a later date to oxidize or hydrolyze polyvinyl benzoate and identify the products so obtained. Oxidation should yield *o*-, *iso*-, or *terephthalic* acids if nuclear addition occurs. Hydrolysis should yield a 1,2-glycol arrangement on the residual polymer chain if tertiary α -hydrogens on the chain are replaced.

Though no direct analysis of the reactivity of vinyl benzoate and its derivatives with growing free radicals was made in this study, it will be noted from Tables I and II that interrupted copolymerizations of vinyl acetate with vinyl benzoate, vinyl *p*-chlorobenzoate, and vinyl *p*-methoxybenzoate produced copolymers which were always richer in vinyl benzoate or its derivatives than the monomer charge. These results might also be interpreted as support for the theory that vinyl benzoate is bifunctional in polymerization.

Additional evidence supporting the bifunctionality of unsaturated benzoic esters is the observation made in these laboratories by Dr. E. C. Chapin that polymers containing methyl *p*-vinylbenzoate are cross-linked. Similar activation of a ring double bond would be expected in this case.

An interesting observation was made that the emulsion copolymerization of vinyl acetate with vinyl *o*-chlorobenzoate, *p*-chlorobenzoate, *p*-methoxybenzoate, *m*-toluate, and *p*-toluate proceeded much more rapidly than vinyl acetate-vinyl benzoate copolymerizations. Since over-all rate of polymerization in emulsion is quite sensitive to emulsifier type and concentration it is not certain whether any conclusion regarding the influence of substituents on the rate of polymerization of vinyl benzoate can be drawn. However, it may be pointed out that the calculated polarizing forces⁴ in dynes $\times 10^{-4}$ of $-\text{Cl}$ (-0.68), $-\text{OCH}_3$ (-1.21), and $-\text{CH}_3$ (-0.39) substituents are all substantially different from the polarizing force of a $-\text{H}$ substituent (0.45).

As shown in Tables I and II, increasing concentrations of vinyl benzoate or substituted vinyl benzoate in copolymers with vinyl acetate resulted in increasing heat distortion points and flex temperatures of molded specimens. These effects are undoubtedly the consequence of restricted movement of phenyl groups due to steric hindrance.

EXPERIMENTAL

Mass polymerizations of vinyl benzoate and copolymerizations of vinyl benzoate and vinyl acetate were conducted in 4, 8, and 12 oz. French

TABLE I. COPOLYMERS OF VINYL ACETATE AND VINYL BENZOATE

Initial composition, %		Properties of copolymers											
Vinyl acetate	Vinyl benzoate	Temp., °C.	Reaction time, hrs.	Polymerization method	Catalyst	Isolation	Conv., %	Strength, p.s.i. distortion		Izod impact strength, ft.-lb./in. (4)	Analysis of copolymer	% vinyl benzoate in copolymer	Specific viscosity in 2% dioxane
								Tensile	Flexural				
75	25	60	96	Soln. 1/1 benzene	0.1% Bz ₂ O ₂	7% soln. in benzene pptd. in 8 vol. hexane	49.5	6,883	11,760	52	60.60 C { 6.42 H {	27.9	—
50	50	60	144	"	"	"	53.0	6,200	11,000	56	60.53 C { 6.75 H {	55.9	—
25	75	60	168	"	"	"	57.8	4,609	6,990	65	65.32 C { 6.45 H {	77.9	—
90	10	60	336	0.77/1.00 benzene/monomer	"	Monomer removed under vac.	79.2	6,350	14,400	44	69.13 C { 5.55 H {	—	4.45
80	20	60	336	"	"	All mass samples insol.	65.1	7,650	10,650	—	—	—	4.68
90	10	65	168	Mass	"	and cross-linked	—	—	—	—	—	—	Swells in solvents
75	25	65	336	"	"	"	—	—	—	—	—	—	"
50	50	65	336	"	"	"	—	—	—	—	—	—	"
25	75	65	336	"	"	"	—	—	—	—	—	—	"
90	10	70	48	Emulsion 0.25% K ₂ S ₂ O ₈ Acto 600	0.5% K ₂ S ₂ O ₈	Steam-distilled, dried	29.4	5,600	12,700	42	—	—	—
60	40*	65	336	Mass	0.05% Bz ₂ O ₂	All samples cross-linked and insol.	—	—	—	—	—	—	Swells in solvents

A.S.T.M. designations: (1) D638-46T; (2) D790-45T; (3) D648-45T; (4) D256-47T.

* 7 charges using different cuts of vinyl benzoate.

TABLE II. COPOLYMERS OF VINYL ACETATE AND VINYL BENZOATE DERIVATIVES

Initial composition, %			Properties of copolymers												
Derivs. of Vinyl acetate	Vinyl benzoate	Temp., °C.	Reaction time, hrs.	Polymerization method	Catalyst	Isolation	Conv., %	Strength, p.s.i.		Oil bath heat distor- tion point, °C. (3)	Izod impact strength, ft.-lb./in. (4)	Analysis of copolymer	Specific viscosity		
								Ten- sile (1)	Flex- ural (2)						
75	25	vinyl <i>p</i> -methoxybenzoate	60	2	Interpreted mass	0.05% BzO ₂	Residual monomer removed under vacuum	20.6	—	—	50.0	—	C ₂ { ^{59.40} H ^{59.32} H}{ ^{6.99} ^{6.89}	30.9	—
50	50	"	60	48	Mass	"	Clear, colorless, cross-linked	—	—	—	—	—	—	—	Swells in solvents
90	10	"	60	48	"	"	"	—	—	—	—	—	—	—	Swells in solvents
90	10	"	70	24	Emulsion	0.05% K ₂ S ₂ O ₈	Steam-distilled, direct	74.0	6,550	14,000	44.5	1.12 un-notched	—	—	2.2 in 2% dioxane
90	10	"	60	96	Soln. 1/2 monomer/benzene	0.25% Ac ₂ O 600	dried under vac.	0.0	—	—	—	—	—	—	—
90	10	"	60	96	Soln. 1/2 monomer/benzene	0.006% Bz ₂ O ₃	Pptd. in hexane	—	—	—	—	—	—	—	—
90	10	vinyl <i>p</i> -chlorobenzoate	80	6	Emulsion 2/1 H ₂ O/monomer	0.1% K ₂ S ₂ O ₈ 1% aerosol OT	Steam-distilled, frozen, filtered, dried under vac., insol. in all solvents tried	83.1	4,100	8,350	<i>T_F</i> = 28°C.	Cl ₂ { ^{2.82} ^{2.71}	14.2	—	—
75	25	"	80	4	"	"	"	92.3	5,800	11,800	<i>T_F</i> = 33°C.	3.1 un-notched	—	—	Swells in solvents
50	50	"	80	9	"	"	Worked up as above, sol. in dioxane	92.0	6,825	14,000	<i>T_F</i> = 56°C.	1.7 un-notched	—	—	22.75 in 2% di-oxane
90	10	vinyl <i>p</i> -phenylbenzoate	70	720	Mass	0.05% Bz ₂ O ₃	Product clear, cross-linked	—	—	—	—	—	—	—	Swells in solvents
80	20	"	70	720	"	"	"	Low	—	—	—	—	—	—	—
70	30	"	70	720	"	"	"	"	—	—	—	—	—	—	—
90	10	vinyl <i>o</i> -chlorobenzoate	80	3	Emulsion	0.1% K ₂ S ₂ O ₈ 0.5% aerosol OT	Steam-distilled, frozen, filtered, dried under vac.	100.0	5,600	10,900	10	Same as charge	—	—	9.53 in 2% acetone
75	25	"	80	3	"	"	"	100.0	6,700	13,300	10	Same as charge	—	—	Swells in solvents
90	10	vinyl <i>p</i> -toluate	70	6	"	"	"	94.0	3,300	10,700	—	—	—	—	"
90	10	vinyl <i>m</i> -toluate	80	3	"	0.1% K ₂ S ₂ O ₈ 0.25% aerosol OT	"	100.0	—	—	—	—	—	—	"
75	25	"	85	4.5	"	0.3% K ₂ S ₂ O ₈ 0.5% aerosol OT	"	97.5	—	—	—	—	—	—	"

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square bottles using 0.05% benzoyl peroxide as catalyst in an oven regulated at $65^{\circ}\text{C.} \pm 0.5^{\circ}$ (Table I). Each of the seven distillation fractions of vinyl benzoate (n_D^{25} : 1.5261, 1.5262, 1.5268, 1.5265, 1.5269, 1.5268, and 1.5268) was mixed with sufficient freshly distilled vinyl acetate in French square bottles, to produce 60% vinyl acetate solutions; the benzoyl peroxide was added; and the air above the liquid was removed by a nitrogen flush. The bottle caps containing aluminum foil interliners were rapidly screwed in place and the bottles were placed in the $65 \pm 0.5^{\circ}$ oven for two weeks. At the end of this time the hard copolymer was removed and attempts to dissolve it in acetone, ethyl acetate, dioxane, chloroform, and carbon tetrachloride were made. Only swollen gels were obtained.

Using the composite refractionated vinyl benzoate and redistilled vinyl acetate mixtures containing 10, 25, 50, and 75% vinyl benzoate and 0.05% benzoyl peroxide were allowed to polymerize in an oven at $65 \pm 0.5^{\circ}\text{C.}$ The first sample was hard after one week and after removal was found to be cross-linked and swollen by conventional solvents. The other samples were hard after two weeks (0.1% benzoyl peroxide added after one week) and were also found to be cross-linked. Vinyl benzoate (100 g.) was mass polymerized with 0.1% benzoyl peroxide for three days at 70°C. and two days at 110°C. The hard polymer obtained formed swollen gels in dioxane, benzene, ethyl acetate, ethylene chloride, and acetone.

Soluble copolymers of vinyl acetate and vinyl benzoate were readily prepared by conducting the copolymerizations in benzene or dioxane solutions. Vinyl acetate-vinyl benzoate mixtures containing 25, 50, and 75% vinyl benzoate and 0.1% benzoyl peroxide were combined with equal weights of benzene and allowed to copolymerize at 60°C. for four days. The benzene solutions were diluted to approximately 7% concentration of copolymer and unreacted monomer and poured with stirring into eight volumes of hexane. The flocculent precipitates obtained were filtered, washed with hexane, and dried. Use of a more concentrated solution of resin or less hexane resulted in a sticky precipitate. A conversion of 49.5% to copolymer was obtained when the initial monomer contained 10% vinyl benzoate. The copolymer produced in this way was readily soluble in dioxane, benzene, ethyl acetate, alcohol, and acetone. As shown in Table I, molded specimens produced from these copolymers possess excellent tensile and flexural strengths.

Copolymerization of a mixture of 80% acrylonitrile-20% vinyl benzoate at a final water/monomer ratio of 2/1 with 0.2% potassium persulfate as catalyst and 0.3% Acto 600 as emulsifier produced a 48% conversion to copolymer. The monomer mixture was added to the reaction mixture over a three hour period at 75°C. Solutions of this resin in dimethylformamide were somewhat gel-like, indicating polymer branching.

Mass copolymers of vinyl acetate (90, 50)-vinyl *p*-methoxybenzoate (10, 50) were prepared, using the same technique as described for the co-polymerization of vinyl acetate and vinyl benzoate. These copolymers were also cross-linked and yielded swollen gels in conventional

solvents. A soluble copolymer was obtained by interrupting a mass copolymerization of 75% vinyl acetate–25% vinyl *p*-methoxybenzoate at 20.6% conversion. An emulsion copolymer containing 10% vinyl *p*-methoxybenzoate could be compression-molded in spite of some indication of copolymer branching, because of the finely subdivided state of the resin. The molding showed evidence of poor flow and fusion. This copolymer appeared to be soluble in dioxane, acetone, and benzene and a specific viscosity of 2.2 in 2% dioxane was obtained.

Copolymers of vinyl acetate (85.8, 70.6, 45.7)–vinyl *p*-chlorobenzoate (14.2, 29.4, 54.3) were prepared in emulsion by addition of the monomer mixture during polymerization as shown in Table II. Dioxane, ethyl acetate, acetone, chloroform, carbon tetrachloride, and benzene solutions of these copolymers were quite gel-like. Compression moldings of these resins possessed imperfect surfaces and tended to distort if removed from a hot mold. This behavior is taken as further evidence of chain branching and cross-linking. A specific viscosity value of 22.75 obtained with the 54.3% vinyl *p*-chlorobenzoate copolymer is probably not significant because of possible presence of traces of gel. Copolymers of vinyl acetate and vinyl *o*-chlorobenzoate exhibited similar behavior (Table II). A copolymer containing 25% vinyl *o*-chlorobenzoate swelled in acetone, benzene, carbon tetrachloride, cyclohexanone, dioxane, and cyclohexanone. A copolymer containing 10% vinyl *o*-chlorobenzoate appeared to give gel-free solutions, but moldings showed definite evidence of poor flow and fusion.

A copolymer of 90% vinyl acetate–10% vinyl *p*-toluate was prepared in emulsion. This resin was also swollen by the various solvents mentioned above, but could be molded (Table II).

Copolymers of vinyl acetate (90, 75)–vinyl *m*-toluate (10, 25) were also prepared in emulsion, but characteristic swelling in the usual solvents was noted.

Vinyl benzoate used in this study was prepared by two independent methods. Most of the vinyl benzoate utilized was made by the continuous vapor phase reaction of acetylene and benzoic acid over a catalyst composed of zinc acetate supported on activated carbon. In addition, a sample was prepared for comparative purposes by the acidolysis of vinyl acetate with benzoic acid in the presence of mercuric acetate.¹

The various nuclearly substituted vinyl benzoates were also prepared by the acidolysis of vinyl acetate with the substituted benzoic acid in the presence of mercuric acetate⁵ (Table III).

In a typical preparation a 1-liter flask was charged with 236 g. (1.51 moles) of *p*-chlorobenzoic acid, 258 g. (3.0 moles) of vinyl acetate, 5 g. of mercuric acetate, 0.5 cc. of concentrated sulfuric acid, and 7 g. of hydroquinone. The mixture was refluxed on a water bath for thirty-six hours. The *p*-chlorobenzoic acid was completely dissolved during this period. The resulting solution was then distilled, removing the excess vinyl acetate and the ethylidene diacetate under reduced pressure. The product boiling

TABLE III

Compound	Yield, %	B.p., °C.	n_D^{25}	M.p., °C.
Vinyl <i>o</i> -chlorobenzoate	28	115 (12 mm.)	1.5440	-21
Vinyl <i>p</i> -chlorobenzoate	32	122 (20 mm.)	—	49-50
Vinyl <i>p</i> -methoxybenzoate	15	140 (30 mm.)	—	57.5-59.0
<i>Analysis:</i> Calcd. for $C_{10}H_{10}O_2$: C, 67.45%; H, 5.62%. Found: C, 67.55%; H, 5.74%.				
Vinyl <i>p</i> -phenylbenzoate	52	169 (3.5 mm.)	—	50-51.5
<i>Analysis:</i> Calcd. for $C_{15}H_{12}O_2$: C, 80.33%; H, 5.39%. Found: C, 80.36%; H, 5.26%.				
Vinyl <i>m</i> -toluate	27	102 (11 mm.)	1.5246	—
<i>Analysis:</i> Calcd. for $C_{10}H_{10}O_2$: C, 74.08%; H, 6.17%. Found: C, 74.12%; H, 6.39%.				
Vinyl <i>p</i> -toluate	32	103 (11.5 mm.)	1.5268	—
<i>Analysis:</i> Calcd. for $C_{10}H_{10}O_2$: C, 74.08%; H, 6.17%. Found: C, 74.06%; H, 6.05%.				

at 122-123°, at 20 mm. pressure was cooled. The solidified mass was recrystallized from dilute ethanol. The purified product so obtained had a melting point of 49 to 50°C. and was identified as vinyl *p*-chlorobenzoate. A yield of 32% was obtained.

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Summary

Branching and cross-linking are noted in emulsion and mass polymerizations involving vinyl benzoate and nuclearly substituted vinyl benzoates. A theory is proposed to account for this phenomenon based on free radical addition to the benzoate nucleus. Six new vinyl esters of substituted benzoic acids are described.

Résumé

La polymérisation en émulsion et en masse du benzoate de vinyle et de benzoates de vinyle substitués dans le noyau est caractérisée par la ramification et le pontage des chaînes. Une théorie est présentée pour expliquer ces phénomènes, en se basant sur l'addition du radical organique au noyau benzénique. Six esters vinyliques nouveaux, dérivés d'acides benzoïques substitués, sont décrits.

Zusammenfassung

In Emulsions- und Massenpolymerisationen von Vinylbenzoat und Kern-substituierten Vinylbenzoaten werden Verzweigungen und Querverbindungen beobachtet. Es wird eine Theorie vorgeschlagen, die dieser Tatsache Rechnung trägt, und die auf Frei-Radikal Anlagerung an den Benzoatkern begründet ist. Sechs neue Vinylester von substituierten Benzoesäuren werden beschrieben.

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