

Poly(vinyl-*trans*-benzalacetophenone)*

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The effect of light, particularly ultraviolet radiation, upon various organic compounds containing the cinnamoyl or styryl ketone group has been studied extensively.¹ Polymeric materials containing cinnamic ester groups have been prepared and their sensitivity to ultraviolet radiation, with or without various added sensitizers, has been described.² The property shown by these polymers of becoming insoluble when irradiated has prompted their investigation for possible technical applications.

Benzalacetophenone and its derivatives and homologs are known to undergo a self-addition reaction, at the styryl double-bond, to give a variety of products, including cyclic dimers and some polymeric substances. Thus polymeric benzalacetophenone-like compounds should behave in a manner similar to poly(vinyl cinnamate) in their response to ultraviolet irradiation. It seemed of interest to prepare such polymers and to compare their light sensitivity to that of poly(vinyl cinnamate).

A poly(vinylbenzalacetophenone) was considered as being perhaps the simplest polymer to synthesize having a benzalacetophenone group. The most successful synthetic route consisted in first preparing poly(vinylacetophenone) from polystyrene, followed by interaction with an aromatic aldehyde such as benzaldehyde. This sequence produced poly(vinylbenzalacetophenone) of considerable purity, but accompanying side reactions had to be suppressed to avoid insolubilization. Under carefully controlled preparative conditions, a high degree of substitution was obtained without insolubilization.

EXPERIMENTAL

Preparation of Poly(vinylacetophenone)

Poly(vinylacetophenone) was prepared by a modification of a procedure described by Kenyon

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and Waugh.³ The polystyrene used was a commercial sample having $\{\eta\}$ in chloroform of 1.06 ($c = 2.5$ g./l.) The modification introduced involved the isolation of the acetylated polystyrene-aluminum chloride complex by filtration and air drying before decomposition of this complex by water. After thorough washing, the finely divided polymer was dried and then precipitated into agitated water from a filtered, dilute acetone solution. The white, fibrous polymer was washed with water and dried.

ANAL.: Calcd. for $C_{10}H_{10}O$: C, 82.1; H, 6.9. Found: C, 82.3; H, 7.0.

Condensation of Poly(vinylacetophenone) with Benzaldehyde

This condensation was investigated under three different conditions, using (a) alkaline catalysis, (b) acidic catalysis, and (c) refluxing in acetic anhydride solution. All three methods are reported in the literature⁴ to give benzalacetophenone by condensing acetophenone with benzaldehyde.

Alkaline catalysts (sodium hydroxide, piperidine, trimethyl benzylammonium hydroxide) readily catalyzed the condensation of poly(vinylacetophenone) with benzaldehyde, but the reaction was difficult to control. The proper choice of reaction conditions was very critical if insolubilization of the polymer was to be avoided. [This was also found to be true in attempting to prepare reaction products of aromatic aldehydes with poly(methyl vinyl ketone) and poly(methyl isopropenyl ketone).] Refluxing poly(vinylacetophenone) with benzaldehyde in acetic anhydride solution was generally unsatisfactory, for the reaction rate was slow and a certain amount of polymer degradation was encountered.

The best method of preparation was found to be acid-catalyzed.⁵ The reaction was slow at room temperature and while it was not free from insolubilizing side reactions, it was reproducible and easily controlled. Concentrated sulfuric acid

was the catalyst used. Preliminary experiments were run in glacial acetic acid solution. Table I shows the extent of reaction (degree of substitution) obtained in a time-series run at room temperature (25°). To a solution of 10.0 g. of poly(vinylacetophenone) dissolved in a mixture of 190 g. of glacial acetic acid and 25.0 g. of benzaldehyde was added 10.0 g. of a 10% (by weight) solution of concentrated sulfuric acid in glacial acetic acid. After standing in the dark for the reaction period indicated, each sample was poured into about 500 ml. of stirred ethanol. The pale yellow precipitate was twice reprecipitated thus from methyl ethyl ketone solution by pouring it into ethanol and then drying in the dark at room temperature.

TABLE I

Reaction Products of Poly(vinylacetophenone) with Benzaldehyde in Glacial Acetic Acid Solution

Expt. no.	Reaction time hr.	Mole-% substitution	Solubility
8	4	1.9	Soluble
9	8	7.0	Soluble
10	16	13.9	Soluble
11	24	21.4	Soluble
12	32	—	Poorly soluble
13	40	—	Insoluble

The cinnamoyl content of the products was estimated by infrared absorption measurements. These measurements were based on the assumption that a solution of benzalacetophenone in carbon disulfide would absorb identically with a solution of equivalent strength of completely cinnamoylated polystyrene. This assumption was supported by the fact that absorption bands at 6.03, 7.53, 8.27 and 9.85 μ found in benzalacetophenone appeared at exactly these wavelengths in the cinnamoylated polystyrenes, although absent in pure polystyrene.

It was noticed that, if the isolated polymer was not completely free of traces of sulfuric acid, the originally soluble polymer would soon become insoluble. It was suspected that, in the series, as the composition of the polymer changed during the course of the reaction, it came out of solution. This precipitate, in the presence of the sulfuric acid, would be expected to give insoluble products. In the next series of condensations, two modifications were made: (a) the glacial acetic acid used was substituted by benzaldehyde, and (b) anhydrous sodium acetate was added to the reaction

mixture at the end of the reaction period to destroy the sulfuric acid catalyst. Methanol was substituted for ethanol as the precipitant. The relationship between the reaction time (at 25°), the degree of substitution and the sensitivity value⁶ are indicated in Table II.

TABLE II

Reaction Products of Poly(vinylacetophenone) with Excess Benzaldehyde

Expt. no.	Reaction time, hr.	Mole-% reaction	Sensitivity value
14	4	14	32
15	8	28	130
16	16	43	350
17	24	59	650
18	48	88	1000
19	96	100	1400

The polymers described in Table II were all soluble in a number of different solvents, a more complete list of which may be found in Table III.

The preparative conditions used in the case of Experiment No. 19 have been repeated several times, including several multikilogram batches, with the same result. A typical elementary analysis of such a sample is:

ANAL.: Calcd. for C₁₇H₁₄O: C, 87.15; H, 6.02. Found: C, 87.0; H, 6.5.

TABLE III

Solubilities of Poly(vinyl-*trans*-benzalacetophenone)

Soluble in	Swells in	Insoluble in
Benzene	Toluene	Ethanol
Tetralin	Xylene	Methanol
Trichloroethylene	Decalin	Butanol
Ethylenedichloride		2-Ethoxyethanol
Chloroform		2-Methoxyethanol
Chlorobenzene		Carbon tetrachloride
2-Methoxyethyl acetate		Glacial acetic acid
1,2-Dimethoxyethane		Acetonitrile
2-Ethoxyethoxyethyl acetate		Acetic anhydride
Ethylene glycol		
monobenzyl ether		
Furfuraldehyde		
Tetrahydrofurane		
Benzyl alcohol		
Tetrahydrofurfuryl alcohol		
Furfuryl alcohol		
Dioxane		
Anisole		

DISCUSSION

The preparation of poly(vinyl-*trans*-benzalacetophenone) as just described demonstrates again the need for reaction conditions which promote the desired reaction and at the same time suppress undesirable side reactions when dealing with polymeric reactants. The base-catalyzed condensation of poly(vinylacetophenone) with benzaldehyde is apparently accompanied by side reactions which insolubilize the polymer. It is well known that in the alkali-catalyzed reaction between acetophenone and benzaldehyde a Michael-type condensation

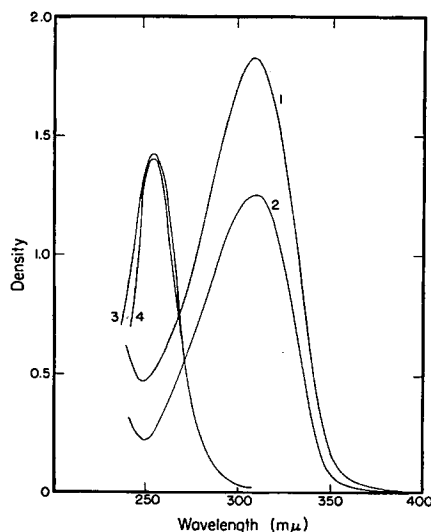


Fig. 1. Ultraviolet absorption spectra of poly(vinylacetophenone) and poly(vinyl-*trans*-benzalacetophenone) with nonpolymeric reference compounds used as models. (1) Poly(vinyl-*trans*-benzalacetophenone), $1 \times 10^{-4} M$ in CHCl_3 . (2) *trans*-*p*-Ethylbenzalacetophenone, $5 \times 10^{-5} M$ in CHCl_3 . (3) Poly(vinylacetophenone), $1 \times 10^{-4} M$ in CHCl_3 . (4) *p*-Ethylacetophenone, $5 \times 10^{-5} M$ in CHCl_3 .

competes with the reaction producing benzalacetophenone.⁷ Thus polymerized vinylbenzalacetophenone entities on one polymer molecule could add to an active methyl group of a polymerized vinylacetophenone unit on another chain molecule under alkaline catalysis.

The crosslinking reaction encountered in the sulfuric acid-catalyzed condensation is, at present, obscure. In solutions of moderate concentration, it is apparently suppressed, but in concentrated solution or in the solid form in the presence of strong sulfuric acid, the poly(vinylbenzalacetophenone) becomes insoluble; hence, the necessity for the neutralization of the acid catalyst prior to the isolation of the polymer.

The characterization of the polymeric condensation product was based largely on the evidence supplied by Figure 1 and the analytical data given. The reference compound with which the comparison was made was the *trans* isomer of 4'-ethylbenzalacetophenone.⁸ Figure 1 shows the ultraviolet absorption curves of this reference compound and the poly(vinyl-*trans*-benzalacetophenone) as well as those of the poly(vinylacetophenone) and *p*-ethylacetophenone. The absorption maxima of these two comparisons are identical in each case but the intensity of absorption is higher in the case of the nonpolymeric materials. This phenomenon is common in such comparisons between a polymer and a corresponding nonpolymeric model. The curves indicate also that the polymeric vinylbenzalacetophenone is essentially free of unreacted polymerized vinylacetophenone units.

Poly(vinyl-*trans*-benzalacetophenone) resembles poly(vinyl cinnamate) in that it, too, has the remarkable property of becoming rapidly insolubilized on exposure to ultraviolet radiation. A coating of the polymer, 2 to 5 μ thick, when exposed to a carbon arc for a few seconds, will become insoluble in all solvents for the unexposed polymer. The polymer itself may be stored in the dark for years without losing its solubility.

The sensitometric data shown in Table II indicate the effect of increasing styryl ketone content upon the sensitivity to light. Caution must be used in attempting to use these data in comparing

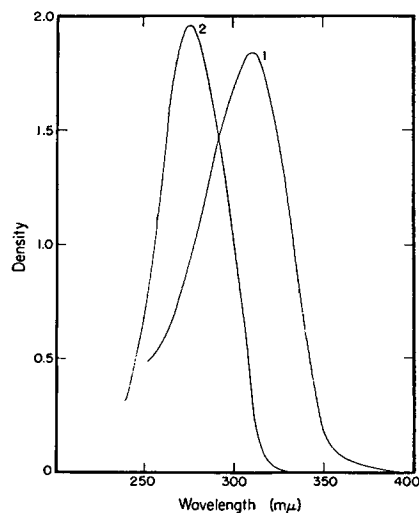


Fig. 2. Comparison of ultraviolet absorption spectra of poly(vinyl-*trans*-benzalacetophenone) with poly(vinyl cinnamate). (1) Poly(vinyl-*trans*-benzalacetophenone), $1 \times 10^{-4} M$ in CHCl_3 . (2) Poly(vinyl cinnamate), $1 \times 10^{-4} M$ in CHCl_3 .

them with similar values obtained for unsensitized poly(vinyl cinnamates). A standard poly(vinyl cinnamate) of known composition and inherent viscosity showed a sensitivity value of 2.2,² but this is not a true indication of the intrinsic light sensitivity. The standard sensitometric test⁵ shows the poly(vinylbenzalacetophenone) to be much more sensitive than poly(vinyl cinnamate), but this apparent higher sensitivity can, to a large extent, be explained by the data shown in Figure 2. The light source used was the same in both cases, and hence the energy output over the range of absorptions shown by the two polymers was similar. The test exposure was made behind a heavy glass plate and also a photographic negative. The film support in the latter, together with the plate glass, filter out a considerable amount of the emitted energy. The absorption of the poly(vinylbenzalacetophenone) at considerably higher wavelengths results in a very much higher sensitivity. This large difference is very much smaller if a cast polymethyl methacrylate (Lucite or Plexiglas) is substituted for the plate glass. A more detailed discussion of this sensitometry lies outside the scope of this investigation.

The polymeric benzalacetophenone resembles poly(vinyl cinnamate) in another respect. The sensitivity of the polymer depends not only upon the proportion of cinnamoyl groups on the polymer chains but also on the molecular weight of the polymer. This is indicated in Table IV.

TABLE IV
Effect of Molecular Weight on Sensitivity

Expt. no.	{ η } of original polystyrene (CHCl ₃ ; 2.5 g./l.)	Sensitivity value
20	0.67	450
21	1.06	1400
22	1.78	Very high, image would not develop completely

Fewer crosslinks per unit weight of polymer are required to effect insolubility of higher molecular weight materials. Not only was this true in the case of poly(vinyl cinnamate) but it was also found to be the case in the insolubilization of polyethylene by high-energy radiation⁹ and in the gelation of polymer solutions by chemical means.¹⁰

Figure 3 shows a plot of the degree of reaction against the reaction time in a series of experiments

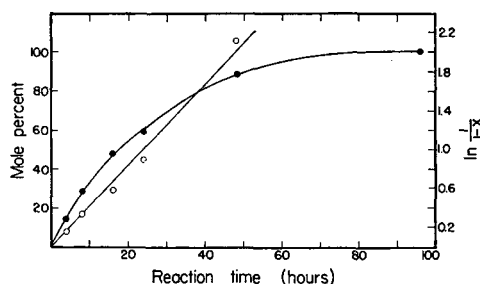


Fig. 3. Reaction rate characteristics of the condensation of poly(vinylacetophenone) with benzaldehyde. (●) The mole per cent of polymerized vinylbenzalacetophenone units in the product as a function of time. (○) Relation between $\ln(1/1-x)$ and reaction time, where x is the mole fraction of vinylacetophenone units which have been converted to vinylbenzalacetophenone units.

where benzaldehyde was used both as a reagent and as a solvent. A plot of the time of reaction (t) against

$$\ln(1/1-x)$$

where x is the mole fraction of vinylacetophenone units in the reaction mixture which have been converted to vinylbenzalacetophenone units in a given time, t , is essentially linear.

The relationship between the mole fraction of polymerized vinylbenzalacetophenone units in the polymer and the photosensitometric response is given in Figure 4. The essentially linear relationship over most of the composition range is interesting in that it differs from poly(vinyl cinnamate) in this respect.² In the case of the polymeric cinnamate, there is a much greater change in solubility characteristics with increasing cinnamate ester formation than is the case of increasing degree of reaction of poly(vinylacetophenone) units with benzaldehyde. The use of a single developing solvent for the irradiated coatings of widely differing solubility characteristics could conceivably

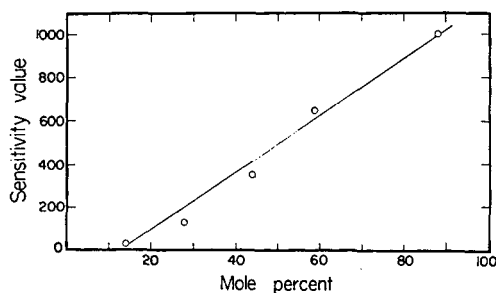


Fig. 4. Relation between polymerized vinyl-*trans*-benzalacetophenone content (mole per cent) and sensitivity value.

produce sensitivity data which may make direct comparisons unjustifiable in the case of partially esterified members. Fully cinnamoylated poly-(vinyl alcohol) has solubility characteristics which closely resemble those of a wide spectrum of compositions derived from poly(vinylacetophenone) and benzaldehyde. These should therefore give fairly representative sensitometric data.

Numerous attempts to increase the sensitivity of poly(vinylbenzalacetophenone) by the addition of various nonpolymeric sensitizing agents were generally unsuccessful, or the increase in sensitivity (expressed as a factor) was relatively low. This is in sharp contrast to poly(vinyl cinnamate) where, under similar test conditions, the response to a number of sensitizers was very strong.²

The sensitometric data reported in this paper were supplied by Earl M. Robertson and the absorption data by Thelma Davis. Their contributions to this work are gratefully acknowledged.

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Synopsis

Polystyrene has been partially or completely modified to contain varying amounts of vinyl-*trans*-benzalacetophenone units in the polymer chain. Acetylation of polystyrene gave a pure poly(vinylacetophenone) which, when condensed with benzaldehyde, produced varying proportions of vinyl-*trans*-benzalacetophenone in the polymer. These styryl ketone polymers are very sensitive to ultraviolet radiation, thin layers becoming insoluble on brief exposure, yet can be stored in the dark for years without change.

Résumé

Le polystyrène a été partiellement ou complètement modifié en incorporant des quantités variables d'unités *trans*-benzalacétophénonnes vinyliques dans la chaîne polymérique. L'acétylation du polystyrène donnait la polyvinylacétophénone qui, condensée avec le benzaldéhyde, fournit des proportions variables d'unités *trans*-benzalacétophénone vinyliques au sein du polymère. Ces polymères styrylcétoniques sont très sensibles à l'irradiation ultraviolette, des couches mêmes devenant insolubles après une courte exposition alors qu'elles peuvent être conservées sous aucun changement pendant des années à l'obscurité.

Zusammenfassung

Eine partielle oder vollständige Modifizierung von Polystyrol wurde durch Bildung verschiedener Mengen von Vinyl-*trans*-benzalacetophenon-einheiten in der Polymerkette durchgeführt. Acetylierung von Polystyrol lieferte ein reines Poly(vinylacetophenon), welches bei der Kondensation mit Benzaldehyd wechselnde Anteile an Vinyl-*trans*-benzalacetophenon im Polymeren bildete. Diese Styrolketonpolymeren sind sehr empfindlich gegen Ultraviolettbestrahlung, so dass dünne Schichten bei kurzer Bestrahlung unlöslich werden; sie lassen sich jedoch im dunkeln jahrelang ohne Veränderung lagern.

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