

Ultraviolet Stabilizing Monomers and Polymers.

I. Synthesis and Polymerization of Phenyl 5-Methacryloxymethylsalicylate*

J. FERTIG, A. I. GOLDBERG, and M. SKOULTCHI,
*Alexander Laboratory, National Starch & Chemical Corporation,
Plainfield, New Jersey*

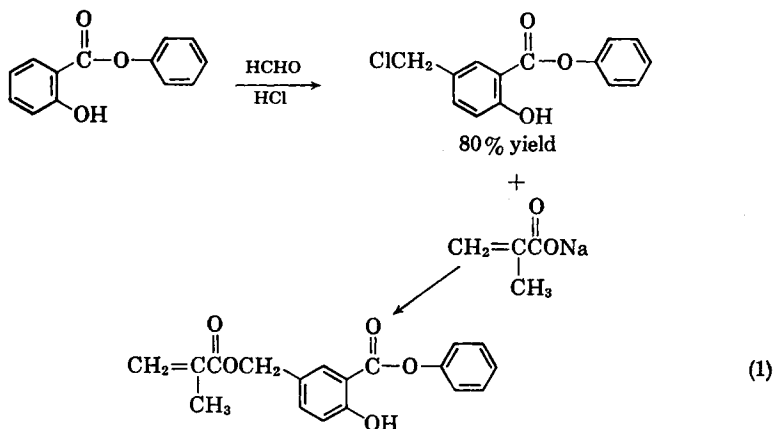
Synopsis

With a view to permanently incorporating ultraviolet stabilizing moieties into polymer systems, monomers containing the phenyl salicylate structure have been prepared and polymerized. Phenyl 5-acryloxymethylsalicylate and phenyl 5-methacryloxymethylsalicylate were prepared by the chloromethylation of phenyl salicylate and subsequent reaction with sodium acrylate or methacrylate. Homopolymers and copolymers of the methacryloxymethyl monomer were prepared and studied. The ultraviolet spectra of the chloromethyl derivative, the monomers, and the homopolymers were essentially similar to that of the starting material, phenyl salicylate. Copolymers of the ultraviolet-absorbing monomers (2%) with vinyl acetate, vinylidene chloride, and vinyl chloride were prepared. The ultraviolet stability of these copolymers was then compared to that of an unstabilized control series and a series containing phenyl salicylate. While there were some differences in the behavior of the copolymerized absorber it was at least as effective as phenyl salicylate in stabilizing the polymers.

The advantage of an ultraviolet stabilizing moiety chemically attached to the substrate has been generally recognized in the past few years. Such problems as migration, volatility on prolonged exposure to exterior conditions, compatibility, and toxicity should be minimized by this approach. Recent patent literature¹ cites examples, wherein vinyl and allyl esters of salicylic acid are copolymerized and thus permanently attached to the polymeric substrate. The use of salicylates as ultraviolet absorbers is well known,²⁻⁶ and phenyl salicylate has, in particular, been extensively used for the stabilization of poly(vinylidene chloride)⁶ and to a more limited extent for poly(vinyl chloride)² and polyolefins.

In this work, the approach to the preparation of ultraviolet absorbing monomers has been to use the phenyl salicylate moiety, and to attach onto it, by fairly simple organic reactions, acrylate and methacrylate groups [eq. (1)].

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These monomers may be readily homopolymerized and copolymerized with a wide range of other vinyl monomers, giving very good yield of polymer with high molecular weight.

MONOMER SYNTHESIS

Phenyl salicylate was chloromethylated in a conventional manner with formaldehyde and concentrated hydrochloric acid with arsenious oxide as catalyst. This gave phenyl 5-chloromethylsalicylate in 80% yield after extraction with acetone. The chloromethyl group has been assigned to the 5 position by analogy with other electrophilic substitution reactions on phenols and derivatives.⁷ The chloromethyl compound was then reacted with sodium acrylate or sodium methacrylate in an acetone-water mixture

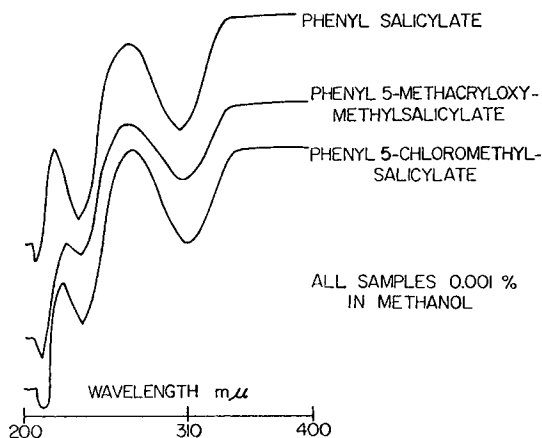


Fig. 1. Ultraviolet spectra of phenyl salicylate and derivatives.

to yield the desired monomers in 80% yield after extraction with methylene chloride. The reaction sequence is shown in eq. (1).

The monomers are viscous, colorless liquids, soluble in a wide range of organic solvents. They polymerized on attempted distillation.

The ultraviolet spectra of phenyl salicylate, the chloromethyl derivative, and the monomers are similar (Fig. 1) and therefore, would be expected to have similar ultraviolet stabilizing properties. The percentage transmission ordinates in Figure 1 have been separated to show the similarity since otherwise the curves would be almost superimposed.

POLYMERIZATION

Most of the work was carried out with the methacrylate since this monomer is easier to prepare and handle. The acrylate tends to polymerize spontaneously.

The homopolymer of phenyl 5-methacryloxymethylsalicylate was prepared by polymerization of the monomer in benzene using benzoyl peroxide as initiator. The polymer was isolated as a white powdery material by precipitation from methanol. The properties of the polymer are shown in Table I.

TABLE I
Poly(Phenyl 5-Methacryloxymethylsalicylate)

Intrinsic viscosity in benzene	0.2
Molecular weight (osmotic)	15,000–20,000
Second-order transition temperature, °C.	58
Soluble:	
Benzene, ethyl acetate, methylene chloride, chloroform, tetrahydrofuran	
Insoluble:	
Methanol, ethanol, cyclohexane, diethyl ether	

The ultraviolet spectrum of the homopolymer is similar to that of the monomer, as shown in Figure 2. Only the region above 300 $m\mu$ is shown for the polymer since its spectrum was taken in benzene which cuts off below 300 $m\mu$.

The possibility of blending small percentages of this homopolymer with other polymers and thus using it as a high molecular weight stabilizer additive has presented itself. This is another way of minimizing migration and volatility problems, though, of course, the polymeric nature increases difficulties due to limited compatibility.

Phenyl salicylate is normally used in the range of 0.5–3% on the polymer as an ultraviolet stabilizer. To compare the ultraviolet stabilizing effect of phenyl salicylate versus the ultraviolet absorbing comonomer, three copolymers of phenyl 5-methacryloxymethylsalicylate (2% by weight) with vinylidene chloride, vinyl chloride, and vinyl acetate were prepared along with six control polymers containing no additive or the equivalent

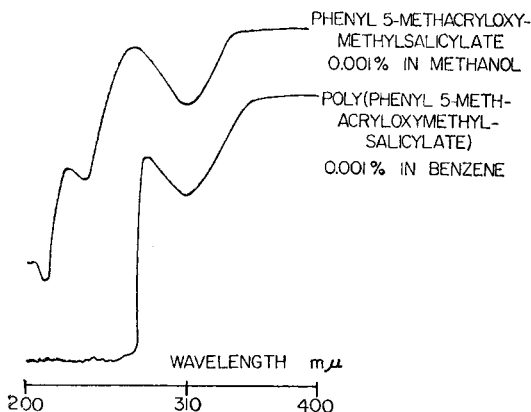


Fig. 2. Ultraviolet spectra of monomer and polymer.

molar amounts of phenyl salicylate (1.37%) added prior to polymerization. For ease of preparation and evaluation, the chloride-containing polymers were prepared with 10 wt.-% ethyl acrylate.

Table II gives data on the polymers prepared. Intrinsic viscosities were comparable in each control series, indicating no appreciable chain transfer effect due to preadded phenyl salicylate.

These polymers were then subjected to ultraviolet exposure under a GE UA-11B lamp. These artificial exposure conditions would not show up the long-term advantages of the permanently attached moieties. However, the purpose here was to confirm that the chemical modification of the salicylate and subsequent polymerization did not detract from its efficiency as an ultraviolet absorber.

TABLE II

Polymer series	Phenyl salicylate, %	Phenyl 5-methacryloxy-methyl-salicylate, %	Intrinsic viscosity ^a
Vinyl acetate	0	0	0.54
	1.37	0	0.55
		2	0.54
Vinyl chloride/ ethyl acrylate ^b	0	0	0.93
	1.37	0	0.87
	0	2	1.30
Vinylidene chloride/ ethyl acrylate ^b	0	0	0.95
	1.37	0	0.97
	0	2	1.04

^a In acetone for vinyl acetate, in tetrahydrofuran for ViCl and ViCl₂ at 30°C.

^b 90/10 by weight.

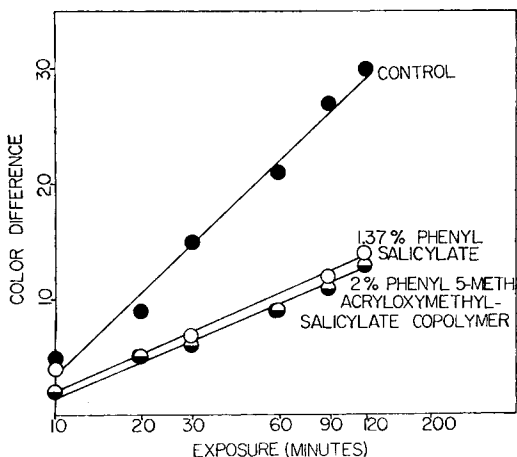


Fig. 3. Ultraviolet exposure of poly(vinylidene chloride).

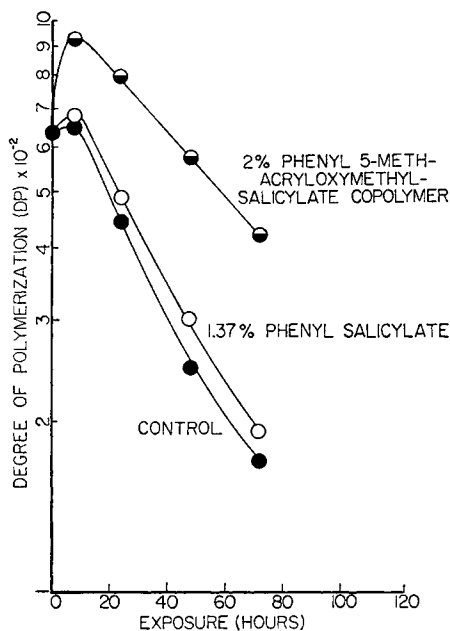


Fig. 4. Ultraviolet exposure of poly(vinyl acetate).

For poly(vinylidene chloride)(Fig. 3) the development of discoloration in the film was measured since this is a convenient criterion for the effect of ultraviolet light on this polymer. Discoloration was plotted versus log time. It can be seen from the graph that the phenyl 5-methacryloxymethylsalicylate and phenyl salicylate are comparable in their protective effect.

Figure 4 shows the poly(vinyl acetate) series. Vinyl acetate degrades under ultraviolet exposure, and molecular weight was used to follow this

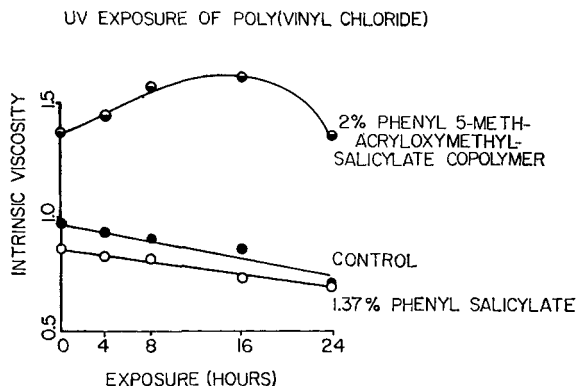


Fig. 5. Ultraviolet exposure of poly(vinyl chloride).

effect. The phenyl 5-methacryloxymethylsalicylate copolymer shows an initial increase in molecular weight, possibly due to some crosslinking of the benzylic methylene hydrogens, followed by a decrease similar to the other two polymers, though the slope is not quite so steep.

Figure 5 shows the result for poly(vinyl chloride). Here the change in intrinsic viscosity for the first 24 hr. of exposure is shown; an increase in molecular weight occurs initially in the methacryloxy copolymer. After this time serious degradation took place in all three polymers, probably due to heat effects.

From these results it can be seen that there are some differences between the behavior of the copolymerized absorber and phenyl salicylate. However, it appears to be at least as effective as the equimolar amount of phenyl salicylate.

EXPERIMENTAL

Preparation of Phenyl 5-Chloromethylsalicylate

A mixture of phenyl salicylate (214 g., 1 mole) commercial grade (91%) paraformaldehyde (109 g., 3.3 mole), 37% aqueous hydrochloric acid (300 g., 3.1 mole), and the catalyst, arsenious oxide (2.04 g.) were heated with stirring for 24 hr. at 100°C. During this time hydrogen chloride gas was passed slowly into the reaction mixture to maintain saturation. After cooling, the lower nonaqueous phase was separated off, dissolved in acetone (100 g.), and allowed to stand overnight over calcium carbonate (10 g.) to remove hydrogen chloride, and a drying agent, calcium sulfate (10 g.). The solution was then filtered and the acetone removed under reduced pressure leaving the product, phenyl 5-chloromethylsalicylate (210 g.) as a colorless viscous liquid.

ANAL. Calc. for $C_{14}H_{13}Cl$: Cl, 13.4%. Found: Cl, 13.1%.

Attempted distillation at 1 mm. pressure resulted in evolution of hydrogen chloride and formation of an uncharacterized polymer.

Preparation of Phenyl 5-Methacryloxymethylsalicylate

A solution of sodium methacrylate (59.4 g., 0.55 mole) is water-acetone (69/31, v/v) was mixed with a solution of phenyl 5-chloromethylsalicylate (131.3 g., 0.5 mole) in acetone (50 ml.) and the mixture heated for 4 hr. at 50°C. The product mix was then poured into a large excess of water, and the lower layer was separated off and dissolved in methylene chloride (200 ml.). The methylene chloride solution was washed several times with water and then dried over magnesium sulfate for 16 hr. The solvent was removed under reduced pressure, leaving the product, phenyl 5-methacryloxymethylsalicylate (124.6 g.) in a yield of 80%. Saponification indicated 96% purity. The monomer contained no chlorine. After chromatography on silica gel, the material was analyzed.

ANAL. Calc. for $C_{18}H_{16}O_5$: C, 69.2%; H, 5.2%. Found: C, 70.5%; H, 5.3%; d_4^{25} 1.5709.

Homopolymerization of Phenyl 5-Methacryloxymethylsalicylate

The monomer (25 g.) was dissolved in benzene (75 g.), and benzoyl peroxide (0.12 g.) was then added. The mixture was refluxed for 6 hr., and the polymeric product was precipitated from methanol as a white powder in 72% yield (18 g.); intrinsic viscosity in benzene, 0.2; osmotic molecular weight 15,000–20,000; T_g , 58°C.

Preparation of Copolymers

Vinyl acetate polymers were prepared by regular solution polymerization at 60% solids in ethyl acetate with azobisisobutyronitrile initiator. The vinyl chloride and vinylidene chloride copolymers were prepared by latex polymerization by use of anionic surfactant systems and potassium persulfate as initiator.

Ultraviolet exposures were carried out on 1 mil dry films with the use of a GE UA 11B lamp at a distance of 2 ft. in a parabolic reflector over a 2-ft. diameter rotating turntable at 40–42°C. A modified reflectance photometer (Photovolt 610) was used to measure discoloration.

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Résumé

En vue d'incorporer d'une façon permanente, dans des systèmes polymériques, des particules stabilisatrices vis-à-vis des radiations ultraviolettes, des monomères contenant la structure du salicylate de phényle ont été préparés et polymérisés. Le 5-acryloxyméthylsalicylate de phényle et le 5-méthacryloxyméthylsalicylate de phényle ont été préparés par la chlorométhylation du salicylate de phényle et réaction subséquente avec l'acrylate ou le méthacrylate de sodium. Des homopolymères et des copolymères du monomère méthacryloxyméthyle ont été préparés et étudiés. Les spectres U.V. du dérivé chlorométhyle des monomères et des homopolymères sont semblables à ceux du matériel de départ, le salicylate de phényle. Des copolymères de ces monomères (2%), absorbant dans l'ultraviolet, avec l'acétate de vinyle, le chlorure de vinylidène et le chlorure de vinyle, ont été préparés. La stabilité à la lumière ultraviolette de ces copolymères a été comparée à une série de contrôle non stabilisée et à une série contenant un salicylate de phényle. Tandis qu'il y avait certaines différences dans le comportement de la substance absorbante copolymérisée, c'était au moins aussi efficace que le salicylate de phényle du point de vue de la stabilisation des polymères.

Zusammenfassung

Mit der Absicht, UV-stabilisierende Einheiten in Polymersysteme fest einzubauen, wurden Monomere, welche die Phenylsalicylatstruktur enthalten, dargestellt und polymerisiert. Phenyl-5-acryloxymethylsalicylat und Phenyl-5-methacryloxymethylsalicylat wurden durch Chlormethylierung von Phenylsalicylat und darauffolgende Reaktion mit Natriumacrylat oder Methacrylat dargestellt. Homo- und Copolymere des Methacryloxymethylmonomeren wurden hergestellt und untersucht. Die UV-Spektren des Chlormethylderivats, der Monomeren und der Homopolymeren glichen im wesentlichen demjenigen des Ausgangsmaterials Phenylsalicylat. Copolymere der UV-absorbierenden Monomeren (2%) mit Vinylacetat, Vinylidenchlorid und Vinylchlorid wurden dargestellt. Die UV-Stabilität dieser Copolymeren wurde dann mit derjenigen einer un-stabilisierten Kontrollserie und einer Phenylsalicylat enthaltenden Serie verglichen. Während im Verhalten des copolymerisierten Absorbers gewisse Unterschiede auftraten, war er doch zumindest für die Stabilisierung des Polymeren so wirksam wie Phenylsalicylat.

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