

Polyesters of Hydroxybenzoic Acids

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INTRODUCTION

One of the first man-made condensation polymers was prepared from *p*-hydroxybenzoic acid by Fisher¹ in 1910. The method of preparation, however, involved a step-wise condensation to a polymer of only four units. Several investigators have subsequently reported the preparation of polyesters from the isomeric hydroxybenzoic acids.²⁻⁵ Only one of these investigators³ was successful in preparing high molecular weight polymers containing only the hydroxybenzoic repeat unit. These polymers were sufficiently high in molecular weight to produce satisfactory fibers and films.

In our study, techniques used in the original work were improved, and the polymers were more fully evaluated. The purpose of this paper is to describe the method of preparation and certain physical and chemical properties of the polymers from *m*- and *p*-hydroxybenzoic acids.

I. PREPARATION OF POLYMERS

A. Starting Materials

The materials used in the polymerization were *m*-acetoxybenzoic and *p*-acetoxybenzoic acids. The melting point of the *meta* isomer was 130.5–131.5°C. and that of the *para* isomer was 178–179°C. The isomers were prepared by acetylating the corresponding hydroxybenzoic acids and were purified by crystallization.

B. Method of Polymerization

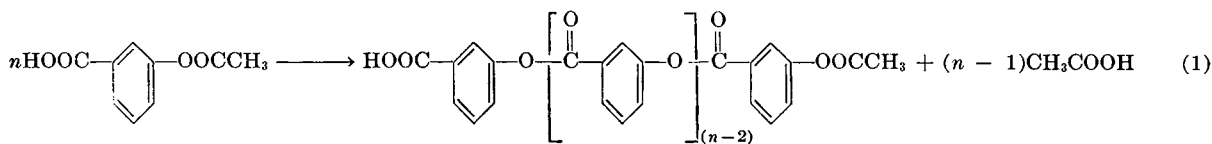
It is difficult to obtain high molecular weight polymers by direct self-esterification of hydroxybenzoic acids. An acid-interchange reaction involving the acetoxy derivative is faster and leads to higher polymers. This reaction proceeds according to eq. (1).

The acetic acid formed is displaced by the aromatic carboxy group, and elimination of the acetic acid results in the formation of a high polymer. This reaction proceeds without a catalyst, but higher molecular weight polymers are formed and a faster reaction results when a catalyst such as magnesium is used. The reaction is preferably carried out at reduced pressure to aid in the removal of acetic acid.

In a typical experiment, 5.5 g. of *m*-acetoxybenzoic acid and 4.5 g. of *p*-acetoxybenzoic acid were placed in a 100-ml., round-bottomed flask provided with an inlet and an outlet for nitrogen, a motor-driven glass stirrer, and an attachment for applying vacuum. The flask was heated by a temperature-controlled metal bath. A small chip of magnesium (about 0.01% on the basis of the amount of monomers) was added to the flask. The contents were melted and heated at 220°C. in a nitrogen atmosphere.

The pressure was lowered to about 60 mm. while nitrogen was admitted slowly, and acetic acid was distilled out. As the melt viscosity of the polymer increased, heat was applied to the bath until a final temperature of 300°C. was reached. The pressure was then reduced to 0.2 mm. In one hour or less the melt viscosity was so high that stirring was no longer effective. The inherent viscosity at this point was approximately 0.5. Inherent viscosities of the polymers were determined with the use of a 60/40 phenol/tetrachloroethane mixture at a concentration of 0.23 g./100 ml.

An additional increase in molecular weight could be obtained by continuing the polymerization in the solid state. This was accomplished by first cooling the polymer under vacuum or in a nitrogen atmosphere, grinding it to a particle size of 0.8 mm. or



less, and soaking it in acetone to promote crystallization. The powdered polymer was then heated at 265°C. for 2–4 hours at 0.1 mm. Copolymers from *m*- and *p*-acetoxybenzoic acid with inherent viscosities as high as 0.9 were prepared by using this technique.

Another procedure which was found especially useful in building up the *m*-hydroxybenzoic acid homopolymer involved the use of a high-boiling, inert solvent. This procedure allowed a longer reaction time and additional build-up in molecular weight by decreasing the viscosity of the reaction mixture. *o*-Terphenyl and a mixture of ditolyl sulfone isomers were satisfactory solvents. The reaction was carried out at 220–250°C. at a pressure which allowed the inert solvent to reflux but not to distill. The polymer obtained by this method could also be further built up in the solid state. The inert solvent was extracted from the melt-polymerized polymer with acetone. The polymer was then ground to a powder and heated for several hours under high vacuum at a temperature below the melting point of the polymer.

In either procedure, stirring the melt greatly facilitated the elimination of acetic acid. Stirrers made of stainless steel were found to be unsatisfactory because of corrosion of the stainless steel and discoloration of the melt. Glass, Teflon, nickel, or titanium stirrers can be used.

Another problem encountered in the copolymerization of *m*- and *p*-acetoxybenzoic acids was that of the difference in rates of reaction. The *para* isomer is more reactive, and its homopolymer is very high melting and very insoluble. Consequently, in a copolymerization, some of the *p*-hydroxybenzoic acid homopolymer or blocks rich in the *para* isomer were being formed continuously; as a result the melt gradually became opaque. This situation can be minimized by the stepwise addition of the *para* isomer during the course of the copolymerization. However, turbid melts are still obtained for copolymers rich in the *para* isomer.

II. PROPERTIES OF POLYMERS

A. Physical State and Color

Poly(*m*-hydroxybenzoic acid) and copolymers containing 65% or more of the *meta* isomer were best made by melt polymerization. Careful exclusion of air during the polymerization limited color formation to a light amber. White powders were obtained by precipitation of these polymers from solution. Copolymers containing 60% or

more of the *para* isomer became solid in the initial polymerization step and had to be built up by solid-phase polymerization. Intermediate compositions could be built up by either melt- or solid-phase polymerization. The solid particles tended to fuse in some compositions during solid-phase polymerization, but built-up continued as long as fairly discrete particles remained.

B. Crystallinity

The polyester from *m*-hydroxybenzoic acid and copolymers containing a major proportion of this isomer are only moderately crystalline; however, the presence of crystallinity in any degree was somewhat unexpected, in view of the general lack of crystallinity in most condensation polymers derived from *meta* isomers. In Figure 1 a powder x-ray diffraction pattern of poly(*m*-hydroxybenzoic acid) is shown.

The degree of crystallinity increased, and the line spacing became identical with that of the *para* isomer as the amount of *para* isomer in the copoly-

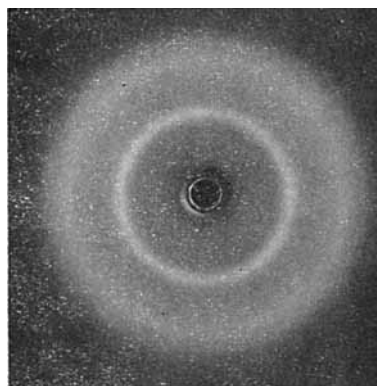


Fig. 1. X-ray diffraction pattern of poly(*m*-hydroxybenzoic acid).

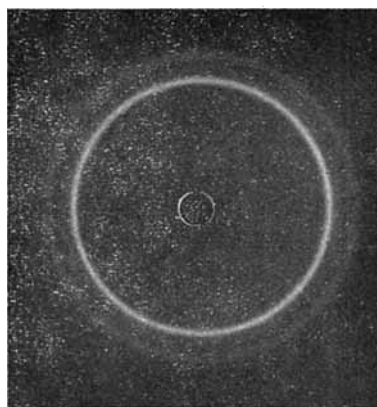


Fig. 2. X-ray diffraction pattern of poly(40 *m*-/60 *p*-hydroxybenzoic acid).

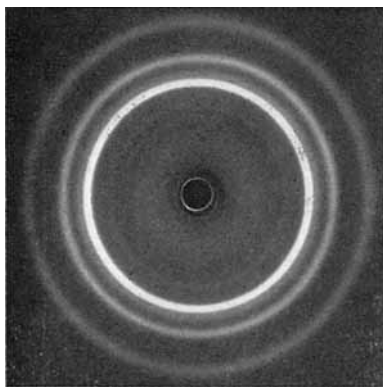


Fig. 3. X-ray diffraction pattern of poly(*p*-hydroxybenzoic acid).

mer was increased. The pattern for a copolymer containing 60% of the *para* isomer is shown in Figure 2. It is evident from Figure 3 that poly(*p*-hydroxybenzoic acid) is very crystalline. Its crystallinity and rigid, aromatic chain structure probably account for its high melting point and insolubility. The x-ray diffraction patterns in each case were taken with the use of nickel-filtered $\text{CuK}\alpha$ radiation.

C. Solubility

Poly(*m*-hydroxybenzoic acid) was soluble in a number of solvents; for example, 1,1,2-trichloroethane, tetrachloroethane, cresol, *N,N*-dimethylaniline, and a mixture of ditolyl sulfone isomers. It was not soluble in methylene chloride or chloroform. Poly(*p*-hydroxybenzoic acid) was found to be insoluble in all solvents tested, including cresol, trifluoroacetic acid, dimethylformamide, and sulfuric acid. Copolymers containing 70% of the *meta* isomer were still soluble in tetrachloroethane. As the amount of *meta* isomer was decreased, the tetrachloroethane solutions became progressively more turbid. This turbidity may have been due in part to blocks of the *p*-hydroxybenzoic acid homopolymer. The copolymer containing 60% of the *para* isomer was almost completely insoluble in tetrachloroethane and was only partially soluble in a 60/40 phenol/tetrachloroethane solution. Tough, flexible films could be cast from tetrachloroethane dopes of the soluble polymers.

D. Molecular Weight

The molecular weight of several poly(*m*-hydroxybenzoic acid) samples was determined from the carboxy group content. Carboxy endgroup equivalents were found by titration of polymer samples dissolved in benzyl alcohol. The reciprocal of car-

boxy group content, expressed in equivalents/gram, is a measure of the number-average molecular weight. The relation between inherent viscosity and molecular weight is shown in Table I.

TABLE I
Relation of Inherent Viscosity to Molecular Weight of Poly(*m*-hydroxybenzoic Acid)

$[\eta]^a$	Carboxy group content, equiv./ 10^6 g.	Mol. wt.
0.33	87.4	11,400
0.42	73.6	13,600
0.48	64.8	14,600
0.59	39.9	25,000

^a Determined in a 60/40 phenol/tetrachloroethane solution at a concentration of 0.23 g./100 ml.

E. Thermal Properties

The melting point of poly(*m*-hydroxybenzoic acid), as observed under polarized light on the hot stage of a microscope, was 185–205°C. This melting point was the range from where flow is first observed to where the crystallinity has completely disappeared. Differential thermal analysis of poly(*m*-hydroxybenzoic acid) gave a value of 176°C. for the crystalline melting point. The sample was heated under vacuum at a rate of 5°C./min. in the determination.

The copolymers were heterogeneous and therefore did not have well-defined melting points. Poly(*p*-hydroxybenzoic acid) appeared to start decomposing above 350°C., but did not melt even when placed on a metal block at 450°C.

The thermal behavior of these polyesters was also investigated by determining the heat-distortion temperature of pressed films under a loading of 5 psi. This information is summarized in Table II. The film of the 40 *meta*/60 *para* copolymer was opaque when pressed at 385°C. Use of a higher temperature to obtain a clear film was unsuccessful.

TABLE II
Effect of Copolymer Composition on Heat-Distortion Temperature^a

Composition of copolymer		Film pressing temp., °C.	Transition temp., °C.	Flow point, °C.
<i>m</i> -Isomer, %	<i>p</i> -Isomer, %			
100	0	215	140	154
55	45	285	154	221
40	60	385	143	>295

^a Samples heated at a rate of 5°/min. at 5 psi.

because the film decomposed. The films were all quenched to prevent crystallization. The transition temperature in each case represented a slight shrinkage of the film and might represent either a crystallization temperature or a second-order transition temperature. The flow point, or yield point, was the temperature at which the film began to elongate rapidly. The flow point of the 55% *meta*/45% *para* copolymer was 149°C. under a loading of 55 psi.

F. Tensile Properties

The tensile properties of pressed films are shown in Table III. It is interesting to compare these values with those reported for poly(Bisphenol A carbonate):⁶ tensile strength, 9,000–10,500 psi; elongation, 60–100%; and tensile modulus, 3.2×10^5 psi. These two types of polyesters are structurally similar in being derived from a phenolic hydroxy group and in having a rigid chain structure.

TABLE III
Effect of Copolymer Composition on Tensile Properties

Composition of copolymer		Tensile strength, psi	Elongation, %	Tensile modulus, psi $\times 10^5$
<i>m</i> -Isomer, %	<i>p</i> -Isomer, %			
100	0	12,100	26	3.0
		10,000	41	2.6
55	45	9,700	7	2.8
		9,180	24	2.5
40	60	10,700	6	3.2

The refractive index of poly(*m*-hydroxybenzoic acid) is 1.623, which is considerably higher than that reported for poly(Bisphenol A carbonate),⁶ namely, 1.584.

G. Chemical Properties

The hydroxybenzoic polyesters differ from the polycarbonates in their hydrolytic stability. The former are relatively sensitive to hydrolysis, compared with the latter. The decreases in inherent viscosity after being heated for 72 hours at 110°C. and 100% R.H. were 90% and 15% for poly(*m*-hydroxybenzoic acid) and poly(Bisphenol A carbonate), respectively.

The hydroxybenzoic acid polyesters are rendered insoluble by heating them in air at 200°C. When a film of the 55% *meta* /45% *para* copolymer cast from tetrachloroethane was heated at 200°C. for 3.5 days in air, very little color developed and the

film was still tough and flexible; however, it was practically insoluble in a 60/40 phenol/tetrachloroethane mixture.

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Synopsis

Polymers and copolymers were prepared from the acetoxy derivatives of *m*- and *p*-hydroxybenzoic acids. Molecular weights of over 20,000 were obtained for poly(*m*-hydroxybenzoic acid) and copolymers containing up to 60% *para* isomer. These polyesters were crystalline, and the degree of crystallinity increased as the *para* isomer content was increased. Blocks of the high-melting, insoluble poly(*p*-hydroxybenzoic acid) tend to form in copolymers containing a high proportion of the *para* isomer because of the difference in reactivity of the two isomers. Copolymers containing at least 55% of the *meta* isomer are soluble in several classes of solvents. The copolymers do not have sharply defined melting points, but have softening temperatures ranging from 150°C. to over 300°C. Tensile strengths of approximately 10,000 psi and elongations of about 6% to 40% were obtained. The polymers were relatively stable to oxidative degradation, but not to hydrolysis.

Résumé

Des polymères et copolymères ont été préparés à partir de dérivés acétylés des acides *m*- et *p*-hydroxybenzoïques. Des poids moléculaires de plus de 20.000 ont été obtenus dans le cas de l'acide poly-*m*-hydroxybenzoïque et des copolymères contenant jusqu'à 60% d'isomère *para*. Ces polyesters sont cristallins et le degré de cristallinité augmente lorsque la quantité d'isomère *para* est augmentée. Des blocs de haut point de fusion, d'acide poly-*p*-hydroxybenzoïque insoluble tendent à se former dans des copolymères contenant une grande proportion d'isomère *para*, à cause de la différence de réactivité des deux isomères. Les copolymères contenant au moins 55% de l'isomère *mé*ta sont solubles dans plusieurs sortes de solvants. Ces copolymères n'ont pas de points de fusion bien définis, mais ils ont de températures de ramollissement comprises entre 150 et 300°C. On a atteint des forces de tension d'environ 10.000 p.s.i. et des elongations variant de 6 à 40%. Ces polymères étaient relativement stables à la dégradation par oxydation mais non à l'hydrolyse.

Zusammenfassung

Aus den Acetoxyderivaten der *m*- und *p*-Hydroxybenzoesäure wurden Polymere und Copolymere dargestellt. Mit Poly-*m*-hydroxybenzoesäure) wurden Molekulargewichte

über 20.000 erhalten und auch Copolymere mit bis zu 60% *para*-Isomeren. Diese Polyester waren kristallin und der Kristallinitätsgrad nahm mit steigendem Gehalt an *para*-Isomeren zu. Bei Copolymerisationsansätzen mit einem hohen Gehalt an *para*-Isomerem besteht, wegen des Unterschieds in der Reaktionsfähigkeit der beiden Isomeren eine Tendenz zur Bildung von Blocks der hochschmelzenden, unlöslichen Poly-(*p*-hydroxybenzoesäure). Copolymere, die zumindest 55% des *meta*-Isomeren enthalten sind in einigen

Klassen von Lösungsmitteln löslich. Die Copolymeren besitzen keine scharfdefinierten Schmelzpunkte, sondern haben Erweichungstemperaturen im Bereich von 150°C bis über 300°C, Zugfestigkeiten von etwa 10000 psi und Dehnungen von etwa 6 bis 40% wurden erhalten. Die Polymeren waren gegen oxydativen Abbau verhältnismässig stabil, nicht aber gegen Hydrolyse.

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