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8

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The Homopolymerization of Hydroxyalkalbenzoic Acid and Hydroxyphenylacetic Acids*

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ABSTRACT

In this study o-, m-, and p-hydroxymethylbenzoic acids, p-hydroxyethylbenzoic acid, p-hydroxyphenylacetic acid and some of the their derivatives were homopolymerized. The procedures used in the synthesis of polymers were direct esterification and transesterification reactions. The direct polyesterification reactions were carried out either by using acidic catalysts such as p-toluenesulphonic acid, antimony trioxide or without using any catalyst. The IR spectra and some physical properties of the homopolymers were examined.

INTRODUCTION

The ever increasing importance of synthetic fibres is the cause of a large-scale research of linear polymers, above all of those types which assure fiber-forming properties, good mechanical properties and a reasonably high melting point. Linear polyesters have become very important polymers in industry since the 1960's. Poly (ethylene terephthalate) has found wide spread application in fibres and films. The successful application of poly (ethylene terephthalate) fibres stimulated a detailed study of this type. In general, the aliphatic polyesters derived from hydroxyacids have found little commercial utility because of their low melting

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points. Polymers derived from aromatic hydroxyacids would appear to be of greater commercial interest because of their potentially high melting points and relatively low cost. Despite many studies on the polymerization of hydroxybenzoic acids, there have been few reports on the homopolymer formation from hydroxyalkylbenzoic acids (1,2,3,4,5,6). Self-condensation reaction of hydroxyphenylacetic acids has not been reported yet.

In this work homopolymerization of *o*-, *m*-, *p*-hydroxymethylbenzoic acids, methyl *p*-hydroxymethylbenzoate, ethyl *p*-hydroxymethylbenzoate, *p*-acetoxymethylbenzoic acid, *p*-acetoxymethylbenzoyl chloride, *p*-hydroxyethylbenzoic acid, methyl *p*-hydroxyethylbenzoate, *p*-hydroxyphenylacetic acid, methyl *p*-hydroxyphenylacetate, *p*-acetoxypheylacetic acid is reported. IR spectra and some physical properties of the homopolymers were examined.

EXPERIMENTAL

Monomers

All of the monomers excluding *p*-hydroxyphenylacetic acid were prepared and purified by the known methods.

Polymers

All polymerizations were carried out in the same general manner. A typical polymerization which yielded poly (*p*-hydroxymethylbenzoic acid) was run as follows:

2 g *p*-hydroxymethylbenzoic acid was placed in a pyrex polymerization tube provided with an inlet and an outlet for CO₂, a magnetic stirrer and an attachment for applying vacuum. The tube was heated by immersing in a *o*-/*m*-phosphoric acid mixture (2:1). *p*-Hydroxymethylbenzoic acid melted at 178–81°C and was heated to 200°C under normal pressure while CO₂ was admitted. After 4 hr the bath temperature was raised to 275°C and held at this temperature for half an hour. The pressure was then reduced gradually to 1–0.5 mm Hg and heating was continued for 9 hr. At the end of the reaction the polymer was allowed to cool. The crude polyester was dissolved in

DMF and poured into excess methanol. The isolated polymer was filtered out and washed with suitable solvents.

PHYSICAL DETERMINATIONS

Molecular Weights

Number average molecular weights of polymer solutions were measured by means of Knauer vapor pressure osmometer using pyridin and DMF as solvents at 60°C and 90°C respectively.

Intrinsic Viscosities

An Ubbelohde-type dilution viscometer was used. An initial polymer solution (less than 1 g/100 ml) was prepared in a 25 ml volumetric flask. 60/40 phenol-1,1,2,2-tetrachloroethane mixture was used as solvent. This solution was used for the first viscosity measurement. Then 10 ml of solvent was added into the viscometer to get a slightly diluted solution for which the second viscosity measurement was done. In the same way, four n_{sp}/c values were obtained at decreasing concentrations, on each polymer. The intrinsic viscosity was determined by extrapolating the straight line of n_{sp}/c versus c plot to $c=0$.

Melting Points

Polymer melting points were determined in a Buchi capillary melting point apparatus.

Infrared Spectra

Infrared spectra of the polymers were obtained on KBr disks by use of a Perkin-Elmer, Model 337, infrared photometer.

Fiber Forming Ability

The ability of the polymers to form fibers was briefly examined and somewhat brittle fibers were manually melt-spun.

RESULTS

Confirmation of the reaction products as polyesters was obtained by infrared spectra. The infrared spectra of the polymers exhibited a sharp carbonyl peak at wavenumber which is characteristic of the carbonyl group of the ester. Infrared absorption band frequencies are seen at Table I.

Table I. Characteristic Infrared Absorptions of the Polymers

Polymer	Wavenumber (cm ⁻¹) (c=0)
Poly (p-acetoxymethylbenzoic acid)	1720
Poly (ethyl p-hydroxymethylbenzoate)	1720
Poly (m-hydroxumethylbenzoic acid)	1702
Poly (methyl p-hydroxyphenylacetate)	1750
Poly (methyl p-hydroxymethylbenzoate)	1720
Poly (p-hydroxyethylbenzoic acid)	1720
Poly (methyl p-hydroxyethylbenzoate)	1730
Poly (methyl p-hydroxyethylbenzoate)	1730
Poly (p-hydroxymethylbenzoic acid)	1750
Poly (p-hydroxyphenylacetic acid)	1750
Poly (p-acetoxymethylbenzoyl chloride)	1720

Melting points, intrinsic viscosities, number average molecular weights of polymers and catalysts used in polymerization is given at Table II. Molecular weights and viscosities of some polymers have been omitted because of solubility problems in the determinations.

Table II. Physical Properties of Polymers

Polymer	Catalysts used in polymerization	Mp, °C	$[\eta]^a$, dl/g	MeX10 ⁻³
1. Poly (p-hydroxymethylbenzoic acid)	p-Toluenesulphonic acid	205-215	0.201	9.764 ^c
Poly (p-hydroxymethylbenzoic acid)	—	220-230	0.216	—
2. Poly (methyl p-hydroxymethylbenzoate)	PbO	220-230	0.281	—
Poly (methyl p-hydroxymethylbenzoate)	Sb ₂ O ₃ -Ca(OCC) ₂ .2H ₂ O	125-130	0.058	—
3. Poly (ethyl p-hydroxymethylbenzoate)	ZnO	210-220	0.240	—
Poly (p-acetoxymethylbenzoic acid)	—	160-175	0.068	1.394 ^c
4. Poly (p-acetoxymethylbenzoic acid)	Metallic Mg	210-220	0.217	9.710 ^c
Poly (p-acetoxymethylbenzoic acid)	p-Toluenesulphonic acid	210-220	0.146	7.419 ^c
Poly (p-hydroxyethylbenzoic acid)	—	140-155	0.108	2.932 ^d
5. Poly (p-hydroxyethylbenzoic acid)	Sb ₂ O ₃	135-150	0.060	—
Poly (p-hydroxyethylbenzoic acid)	p-Toluenesulphonic acid	160-180	0.051	—
6. Poly (methyl p-hydroxyethylbenzoate)	Sb ₂ O ₃ -Ca(AcO) ₂ .2H ₂ O	150-175	0.152	7.078 ^d
7. Poly (m-hydroxymethylbenzoic acid)	—	160-170	0.257	—
Poly (m-hydroxymethylbenzoic acid)	p-Toluenesulphonic acid	135-145	0.81	—
8. Poly (p-hydroxyphenylacetic acid)	—	240-260	0.264	6.558 ^d
Poly (p-hydroxyphenylacetic acid)	p-Toluenesulphonic acid	—	—	—
9. Poly (p-acetoxyphenylacetic acid)	ZnO	20-130	0.057	2.116 ^d
10. Poly (methyl p-hydroxyphenylacetate)	Sb ₂ O ₃ -Ca(AcO) ₂ .2H ₂ O	140-160	0.066 ^c	2.110 ^d
11. Poly (p-acetoxymethylbenzoyl chloride)	—	—	—	—

a) Obtained in phenol-tetrachloroethane (60:40), except where otherwise indicated

b) Obtained in DMF

c) In pyridine

c) In pyridine

d) In DMF

The polymers have varying solubility characteristics in different solvents, as shown in Table III. Most of the polymers are soluble in DMF. The polymers are insoluble in CH_2Cl_2 , CHCl_3 , CCl_4 , C_6H_6 , EtOH and acetone. THF dissolves 5,9 and 10 but not the remaining polymers.

Table III. Solubility Properties of the Polymers

Polymer	Solvents							
	CH ₂ Cl ₂	CHCl ₃	CCl ₄	DMF	C ₆ H ₆	THF	EtOH	Acetone
1	IS	IS	IS	S	IS	IS	IS	IS
2	IS	IS	IS	S	IS	IS	IS	IS
3	IS	IS	IS	S	IS	IS	IS	IS
4	IS	IS	IS	S	IS	IS	IS	IS
5	IS	IS	IS	S	IS	S	S	S
6	IS	IS	IS	S	IS	IS(s)	IS	IS
7	IS	IS	IS	S	IS	IS(s)	IS	IS
8		IS	IS	IS	IS	S	IS	IS
9	S	S	S	S	S	S	IS	S
10	IS	IS	IS	S	IS	S	IS	IS
11	IS	IS	IS	S	IS	IS	IS	IS

a: S=Soluble IS=Insoluble IS(s)=Insoluble but softens.

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ÖZET

Bu çalışmada hidroksialkilbenzoik asitlerden o-,m-, ve p- hidroksimetilbenzoik asitler, p-hidroksietilbenzoik asit; hidroksifenilasetik asitlerden de p-hidroksifenilasetik asidin homopolimerlerinin sentezi yapılarak özellikleri araştırıldı. Polymerlerin sentezinde uygulanan işlemler doğrudan polimerleştirme ve ester değiştirme reaksiyonlarıdır.

Adı geçen asitlerin doğrudan polimerleştirme reaksiyonları hem katalizör kullanılmaksızın hem de p-toluensülfonik asit, antimon trioksit gibi katalizörler kullanılarak yapıldı.

p-Hidroksimetilbenzoik asidin metil ve etil esterlerinin polimerizasyonu yinelen-di, ayrıca p-asetoksiketilbenzoik asit v bunun klörürü de polimerleştirildi. p-Asetoksi-metilbenzoik asitten elde edilen polimerin özellikleri metil p-hidroksimetilbenzoat ve etil p-hidroksimetilbenzoatlardan elde edilen polimerlerinkine yakın özellikler göster-mektedir.

Metil p-hidroksietilbenzoat'tan elde edilen homopolimerin p-hidroksietilbenzoik asitten elde edilen polimere göre daha iyi özelliklere sahip olduğu görüldü.

p-Hidroksifenilasetik asidin homopolimerizasyonunu içeren bir çalışmaya literatürde rastlanmadı. Bu çalışmada p-hidroksifenilasetik asit, metil p-hidroksifenilasetat ve p-asetoksifenilasetik asit polimerleştirildi.

Elde edilen polimerlerin yumuşama ve erime noktaları, sayıca ortalama molekül ağırlıkları, çözünürlükleri ve İR spektrumları gibi özellikleri incelendi.

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