Studies on the Condensation Polymers of Aromatic Acetoxy Carboxylic Acids

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Introduction

Much work has been done by many investigators on the syntheses of polyesters, especially on the polymers of aliphatic hydroxy carboxylic acid and the copolymers of mono- and di-basic carboxylic acids and glycols. But, as for the syntheses of the polymers of aromatic hydroxy carboxylic acid, no systematic study has been made, although Einhorn1) made the dimer of salicylic acid by heating with phosphorus oxychloride and Anschütz2) made the tetramer of it by the same method. This method was used in the present research. In the case of salicylic acid, the formation of the high polymer was not observed. However, in the case of *o*-acetoxy benzoic acid (aspirin), the resin-like substance was obtained. It was considered to be the polymer of salicylic acid, for the violent evolution of acetic acid was observed throughout the reaction with the marked increase of the molecular weight. Starting from this result, the author obtained the high polymers of various kinds of aromatic acetoxy carboxylic acid by heating. The process of the formation of polymers was followed by determining the molecular weight of the resins formed, at several stages of the reaction. From the data obtained, the effect of the position of acetoxy group and carboxyl group on the reactivity of the monomers, was considered. In the case of acetamino carboxylic acids, the formation of the polymer of the high molecular weight by heating was not observed.

Experimental

The monomers used for this research were prepared by the following procedures.

I) *o*-Acetoxy benzoic acid. Aspirin for medical use was purified. M.P. 135°C.

II) *m*-Acetoxy benzoic acid3). *m*-Hydroxy benzoic acid4) was acetylated, using acetic anhydride. M.P. 131°C.

III) *p*-Acetoxy benzoic acid5) was prepared by the action of acetic anhydride on *p*-hydroxy benzoic acid6) which was synthesized from salicylic acid. M.P. 182°C.

IV) 3-Acetoxy naphthoic acid-(2)7) was synthesized from 3-hydroxy naphthoic acid-(2). M.P. 174°C.

V) 2, 4-Diacetoxy benzoic acid8). β-Resorcylic acid9) made from resorcinol by Kolbe-Schmitt method was acetylated. M.P. 134°C.

VI) 3, 5-Diacetoxy benzoic acid10) was made by acetylating 3, 5-dihydroxy benzoic acid11) by acetic anhydride. M.P. 155°C.

VII) *o*-Acetamino benzoic acid5) was made by acetylating *o*-amino benzoic acid. M.P. 180°C.

VIII) *p*-Acetamino benzoic acid12) was prepared by the action of acetyl chloride on *p*-amino benzoic acid. M.P. 253°C.

IX) 2-Acetoxy-4-acetamino benzoic acid. PAS for medical use, was acetylated by acetic anhydride. The product was recrystallized from hot water which contained a small quantity of alcohol, and was identified with the diacetyl compound of PAS by measuring the acetyl value of the product. Yield-70% of the theoretical amount. M.P. 184°C, with decomposition.

The condensation of the monomers shown above was carried out as follows; 10 g. of monomers were heated in a hard test tube of 1.5 cm. diameter during a definite time at the suitable temperature for each compound, which was listed in Table I. The acetic acid evolved in this reaction was carried off on the outside of a test tube by a slow current of dry carbon dioxide.

o-Acetoxy benzoic acid was chosen as the standard substance for comparison. Hence the process of the reaction of this compound was observed in detail at three different temperatures, 170°C, 240°C and 240°C. This monomer reacted smoothly at these temperatures. Contrary to this compound, *m*-acetoxy benzoic acid, *p*-acetoxy benzoic acid and 3, 5-diacetoxy benzoic acid did not react at 200°C. Therefore, the reaction temperature of 240°C was chosen for these compounds. *p*-Acetamino benzoic acid was heated at 300°C, because it reacted smoothly at the higher temperature than its melting point. The polymerization of the other compounds was carried out at two different temperatures (200°C and 240°C), as shown in Table I.

The molecular weight of the resins synthesized in this way was measured by the cryoscopic method using nitrobenzene as the solvent for the

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1) A. Einhorn, *Ber.*, **34**, 2352 (1901).
2) R. Ansuchütz, *Ber.*, **25**, 3506 (1892).
3) A. Heintz, *Ann.*, **153**, 340 (1870).
4) H. Offermann, *Ann.*, **280**, 6 (1894).
5) A. Kauffmann, *Ber.*, **42**, 3482 (1909).
6) H. Kolbe, *J. prakt, Chem.*, (2) **11**, 24 (1875).
7) H. Gradenwitz, *Ber.*, **27**, 2624 (1894).
8) M. Bergmann, *Ber.*, **52**, 379 (1919).
9) A. Clibbens, *J. Chem. Soc.*, **107**, 1494 (1915).
10) F. Mauthner, *J. prakt, Chem.*, **136**, 205 (1933).
11) L. Barth, *Ann.*, **159**, 222 (1871).
12) G. Heller, *Ber.*, **43**, 2574 (1910).

TABLE I

Monomer	Reaction temp. (°C)	Color	Solubility in nitrobenzene	Transparency
o-Acetoxy benzoic acid	170	CL→CL	+	TR
	200	CL→LB	+	
	240	P→B	+	
m-Acetoxy benzoic acid	240	B→B	+	TR
p-Acetoxy benzoic acid	240	W	−	OP
3-Acetoxy naphthoic acid-(2)	200	LB→B	+	TR
	240	B→BB	+	
2, 4-Diacetoxy benzoic acid	200	CL→OY	+	TR
	240	OY→R	+	
3, 5-Diacetoxy benzoic acid	240	LB(F)→B(F)	+	TR
o-Acetamino benzoic acid	200	OY	−	TR
	240	R→BB	−	
p-Acetamino benzoic acid	300	LY	−	OP
2-Acetoxy-4-acetamino benzoic acid	200	RB→BB	−	STR

Color; CL=Colorless, LB=Light brown, P=Pink, B=Brown, W=White, BB=Brownish black, OY=Orange yellow, R=Red, LY=Light yellow. RB=Reddish brown, (F)=Fluorescence.
Solubility; +: Soluble, −: Insoluble.
Transparency; TR=Transparent, OP=Opaque, STR=Semitransparent.

polymers of acetoxy compounds, and phenol as the solvent for the polymers of acetamino compounds.

Results and Discussion

i) **The Properties of Polymers.**—With the increase of the molecular weight, the colors of synthetic resins obtained from *o*-acetoxy benzoic acid, *m*-acetoxy benzoic acid, 3-acetoxy naphthoic acid-(2), 2, 4-diacetoxy benzoic acid and 3, 5-diacetoxy benzoic acid change from colorless to brown (Table I), and their hardness increases, and the solubility decreases. Most of them are soluble in nitrobenzene, phenol and pyridine, but are insoluble in alcohol, ether, chloroform and carbon tetrachloride. The resins of the lower molecular weight slightly dissolve in benzene and acetone, but, with the increase of the molecular weight, they become insoluble in these solvents.

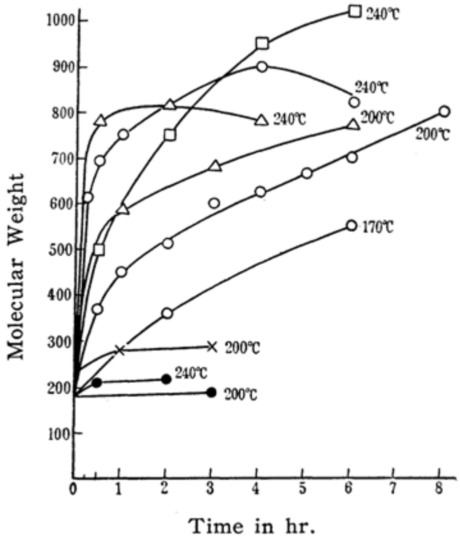
The polymers obtained from *p*-acetoxy benzoic acid and *p*-acetamino benzoic acid were opaque solids and did not dissolve in any solvents. The resins obtained from *o*-acetamino benzoic acid and 2-acetoxy-4-acetamino benzoic acid dissolved in phenol and cresol, but did not dissolve in other solvents.

The polymer (A in Table II) of 2, 4-diacetoxy benzoic acid obtained by heating at 240°C during 4 hrs., and the polymer (B in Table II) of 3, 5-diacetoxy benzoic acid obtained by heating 240°C during 6 hrs. are slightly soluble in nitrobenzene, phenol and pyridine, and the remaining part swells greatly. The degrees of swelling are given in Table II.

TABLE II

DEGREE OF SWELLING (% in volume).

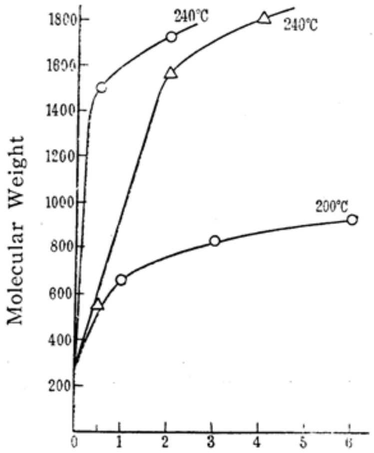
Solvent	Phenol	Nitrobenzene	Pyridine
Polymer (A)	600	430	Soluble
Polymer (B)	280	300	300



○ *o*-Acetoxy benzoic acid
□ *m*-Acetoxy benzoic acid
△ 3-Acetoxy naphthoic acid-(2)
● *o*-Acetamino benzoic acid
× 2-Acetoxy-4-acetamino benzoic acid

Fig. 1

ii) **The Change of Molecular Weight.**—The data obtained by measuring the molecular weight in the course of polymerization are shown in Fig. 1 and Fig. 2.



○ 2,4-Diacetoxy benzoic acid
Δ 3,5-Diacetoxy benzoic acid

Fig. 2

In these figures, the important points will be the maximum value (*p* in Table III) of the degree of polymerization (molecular weight of the polymer/molecular weight of its monomer), which can be obtained in the course of reaction, and the reaction velocity (*V* in Table III) at *t* (time in hour)=0, which is expressed in the ratio of the change of the degree of polymerization to the change of hour. For example, these values of *o*-acetoxy benzoic acid are calculated as follows:

$$P=890/180=5.0$$

$$V(200°\text{C})=\frac{(370/180)-1}{1/2}=2.1$$

As seen from this Table, there is some relation between the chemical structures of monomers and the values of *V*. Namely, almost the same value of *V* are observed for *o*-acetoxy benzoic acid and 2,4-diacetoxy benzoic acid. Furthermore, the value of *V* for *m*-acetoxy benzoic acid is almost the same as the value of *V* for 3,5-diacetoxy benzoic acid, which is smaller than the value of *V* for *o*-acetoxy benzoic acid and 2,4-diacetoxy benzoic acid at 240°C. This fact tells us that the monomers, which have the acetoxy group at the ortho-position to the carboxyl group, react faster than the monomers having the acetoxy group at the meta-position to the carboxyl group. But the value of *P* of *m*-acetoxy compounds is larger than the value of *P* of the corresponding *o*-acetoxy compounds. Therefore, it seems that *m*-acetoxy benzoic acid and 3,5-diacetoxy benzoic acid are suitable for the preparation of the high polymer of aromatic acetoxy carboxylic acid. As for the value of *V* of *p*-acetoxy benzoic acid, it cannot be obtained in this research. Therefore, the stability of *p*-acetoxy benzoic acid cannot be discussed in comparison to *o*-acetoxy compounds. However, considering the fact that *p*-acetoxy benzoic acid does not react at 200°C, it seems that *o*-acetoxy compounds react faster than *p*-acetoxy benzoic acid[13]. As for the values of *V* and *P* of 3-acetoxy naphthoic acid-(2), they are less than those of *o*-acetoxy benzoic acid. Contrary to the case of acetoxy carboxylic acid, the values of *V* and *P* of acetamino compounds are very small. The fact that the color of the product changes rapidly to dark brown may be due to the decomposition of the polymer formed. Therefore, the high polymer will not be obtained from aromatic acetamino carboxylic acid.

TABLE III

Monomer	Reaction temp. (°C)	*V*	*P*	Molecular weight
o-Acetoxy benzoic acid	170 200 240	0.5 2.1 9.7	5.0	895
m-Acetoxy benzoic acid	240	3.6	5.6	1016
3-Acetoxy naphthoic acid-(2)	200 240	1.6 4.7	3.5	811
2,4-Diacetoxy benzoic acid	200 240	1.7 10.6	7.2	1720
3,5-Diacetoxy benzoic acid	240	3.0	7.7	1820
o-Acetamino benzoic acid	200 240	0.03 0.4	1.2	220
2-Acetoxy-4-acetamino benzoic acid	200	0.2	1.2	287

The polymers (A and B in Table II) obtained from 2,4-diacetoxy benzoic acid and 3,5-diacetoxy benzoic acid swell greatly as shown above. These monomers have three functional groups. Therefore, it will be reasonable to assume that their polymers swell, owing to the net work structure formed by the cross linkage, and also their high

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[13] Y. Tsuzuki, This Bulletin, **5**, 282 (1950).

molecular weight. 2, 4-Diacetoxy benzoic acid and 3, 5-diacetoxy benzoic acid will be useful to the formation of the net work structure in the polymer.

Summary

We carried out a fundamental research for synthesizing high polymers of aromatic acetoxy carboxylic acid, and observed the influence of the position of the acetoxy group, and found that *m*-acetoxy benzoic acid, 3, 5-diacetoxy benzoic acid and 2, 4-diacetoxy benzoic acid, are superior as the monomer for the preparation of high polymers of aromatic acetoxy carboxylic acid.

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