Polymer Bulletin 1, 341–345 (1979)

Polymer Bulletin

Polymerization of Anhydro-O-carboxysalicylic Acid

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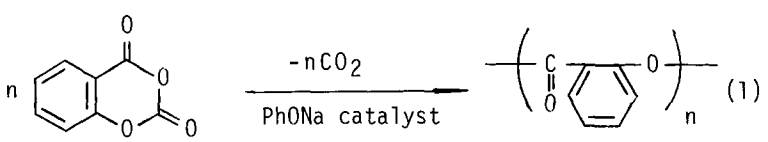
Summary

The present paper describes the anionic ring-opening polymerization of anhydro-O-carboxysalicylic acid 1. At 0°C, the polymerization took place with base catalysts, e.g., sodium phenoxide and pyridine, to give poly-o-benzoate 2, whose molecular weight was of an order of several thousands. A polymer sample melts at 142-150°C and begins to decompose at 260°C. The molecular weight distribution of the polymer was very sharp, especially when the polymerization was carried out at 0°C.

Introduction

This paper is concerned with an anionic ring-opening polymerization of anhydro-O-carboxysalicylic acid 1 to give poly-o-benzoate 2 with the elimination of carbon dioxide.



1 2

Polymerization of 1 has not been reported before the present study. Polymer 2, however, was once prepared by an interfacial polycondensation of salicyl chloride (OGATA and KURAGATA, 1973).

Results and Discussion

Polymerization of Anhydro-O-carboxysalicylic Acid Initiated by Base Catalysts. Monomer 1 was prepared from disodium salicylate and phosgene (DAVIES, 1953). A mixture of monomer 1 and initiator in tetrahydrofuran (THF) or toluene solvent was stirred under nitrogen at a designated temperature. Sodium phenoxide was the most effective among other anionic initiators

0170-0839/79/0001/0341/$01.00

such as sodium methoxide, triethylamine, triphenylphosphine and pyridine. TABLE 1 shows some results of the polymerization of 1 with sodium phenoxide.

TABLE 1

Polymerization of Anhydro-O-carboxysalicylic Acid Initiated by PhONa

No.	Catalyst Conc.* (mole%)	Solvent	Monomer Conc. (mol/l)	Reaction Temp.(°C)	Reaction Time(hr)	Yield (%)	Mol.Wt.**
1	5	THF	0.3	r.t.	1.5	91	1960
2	5	THF	0.3	45	1.5	97	2190
3	5	THF	0.3	60	1.5	96	2270
4	2	Toluene	0.2	0	8	99	5010
5	-	-	Bulk	170	2.5	95	1010
6***	5	Toluene	0.3	45	5.0	78	1570

* Mole percents for monomer 1.

** Determined by vapor pressure osmometry in DMF at 55°C.

*** Pyridine was used as catalyst instead of PhONa.

Polymer structure of 2 was established by ^{1}H NMR and IR spectroscopy, the amount of carbon dioxide evolved during polymerization, and elemental analyses. The ^{1}H NMR spectrum of polymer showed only a multiplet peak at δ 6.3~ 8.2 due to phenyl protons. In the IR spectrum of the polymer (Figure 1), a strong absorption band at 1740 cm^{-1} due to $\nu_{C=O}$ was obserbed.

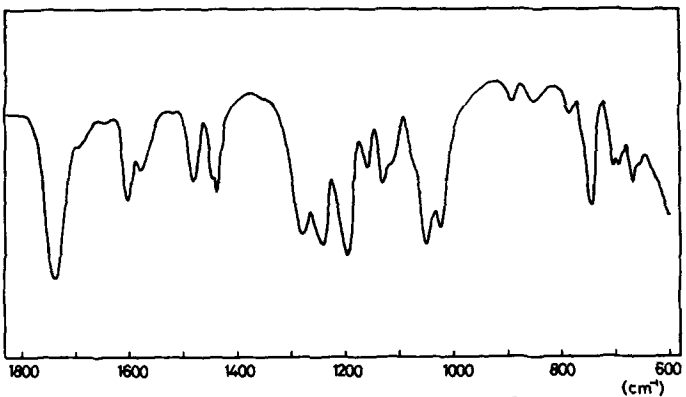


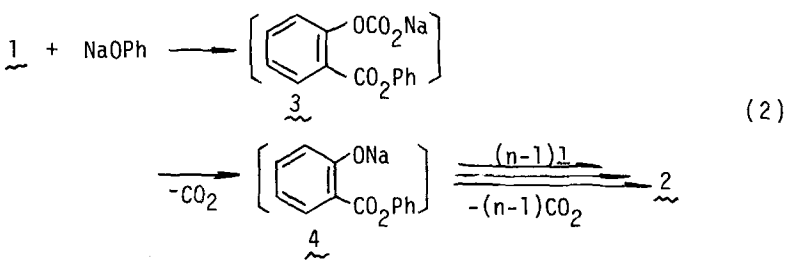
Figure 1. The infrared spectrum of poly-o-benzoate 2 (KBr)

Polymer (sample No.4 in TABLE 1) was white powder and melted at 142-150°C. Anal. Calcd for $(C_7H_4O_2)_n$: C, 70.00; H, 3.36. Found : C, 69.80; H, 3.32.

The evolution of carbon dioxide was followed by gas chromatographic analysis (Figure 2), indicating that the amount of the carbon dioxide was quantitative according to Equation (1).

In the case of pyridine catalyst, 1 was converted quantitatively to polymer 2, but the rate of polymerization was very slow compared to that sodium phenoxide catalyst. For example, with 5 mole percents of pyridine catalyst, the conversions of 1 after 15 and 100 minutes at 45°C were 4 and 45 percents, respectively.

Polymerization Mechanism. From the above findings, the course of the polymerization may be presented by the following scheme, although 3 and 4 have not been isolated as stable species.



(2)

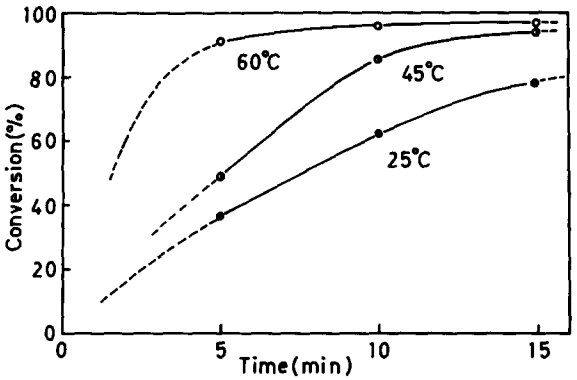


Figure 2. Time-conversion curves followed by the evolution of carbon dioxide during the polymerization of 1 (1.0 mmol) initiated with PhONa (0.05 mmol) in THF (3 ml) at three temperatures.

As to the catalysis of pyridine in this polymerization, the polymerization of sarcosin—NCA was reported, in which a large excess amount of pyridine (12.4 molar ratio toward monomer) was used and a high molecular weight poly-N-methylglycine was produced (KRICHELDORF and BÖSINGER, 1976). The polymerization of 1 was performed under the same reaction conditions.

The molecular weight of 2 thus prepared, however, was very low; 650 by the vapor pressure osmometry. This molecular weight did not increase with a prolonged reaction time.

Molecular Weight Distribution of Polymer 2. By GPC analysis, the molecular weight distribution of polymer 2 was found to be sharp. The polymer prepared with sodium phenoxide catalyst at a low temperature (e.g., curve 4 in Figure 3) showed a $\bar{M}_W/\bar{M}_N$ value of 1.2. The mean length of polymer chains was calculated at 230 Å on the basis of the data of an authentic sample of monodispersed polystyrene with the elution volume of 52.2 ml/count. From the polymer size obtained by GPC, the molecular weight was estimated at 5350 when the Q-value of 2 is assumed to be 23.3. When every initiator molecule causes one propagating chain without chain transfer reaction, the molecular weight of this polymer (sample No. 4, TABLE 1) is calculated at 6000 on the basis of the initiator/monomer molar ratio of 0.02. Three values of molecular weight, i.e., 5010 (by VPO), 5350 (by GPC) and 6000 (calculated from the initiator/monomer ratio), fall in a narrow range. These findings may be taken to assume a living polymerization mechanism.

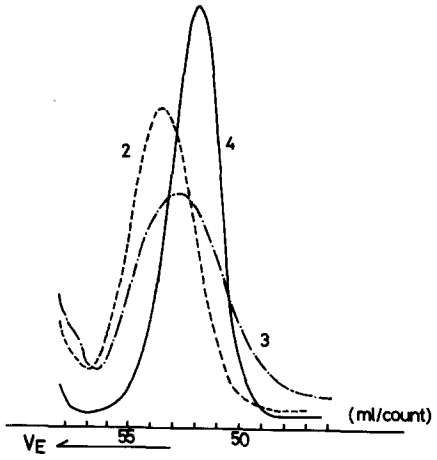


Figure 3. GPC curves of poly-o-benzoate 2. The curve number corresponds to the sample number in TABLE 1. A mixed solvent of m-cresol (15) / chloroform (85) (V/V) was employed. A high-pressure GPC instrument (Toyo Soda Co. Model HLC-802) was used with a elution volume rate of 1 ml/min. at 38°C.

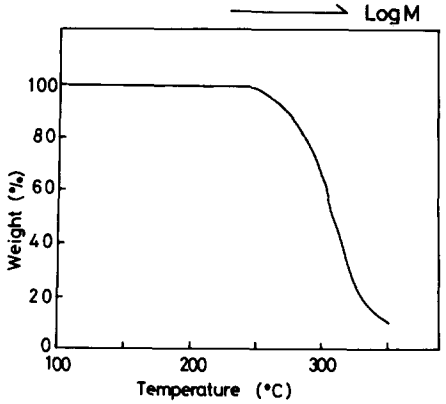


Figure 4. Thermogravimetric analysis of poly-o-benzoate 2 (sample No. 4). The sample was heated at a rate of 20°C/min. in air.

Polymer Properties. Figure 4 shows the thermogravimetric analysis curve of a polymer sample No. 4 in TABLE 1. Although poly-p-benzoate, an isomer of 2, has been known as an excellent heat-resistance resin, polymer 2 begins to decompose at 260°C in air. 2 can be taken as a polymer of salicylic acid, which is known as a strong anti-bacterial. A preliminary test of 2 on the pharmacological activities indicated an anti-bacterial nature with a prologed period, but the activity itself was lower than that of salicylic acid.

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Received January 3o, 1979