

# Synthesis of Poly(ester sulfoimide) from Dichlorocarbonylimide of Disaccharindicarboxylic Acid and Aromatic Diols

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**ABSTRACT:** A new chlorocarbonylimide of disaccharindicarboxylic acid was synthesized by condensation of imides of saccharin-6-carboxylic acid with alkyl- and alkylaryl bishalogenides. Poly(ester sulfoimide), soluble in organic solvents, was synthesized by polycondensation of chlorocarbonylimide with bisphenol. DTA and TGA investigations have shown that poly(ester sulfoimide)s were sta-

ble at temperatures up to 300°C–345°C. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1687–1691, 2006

**Key words:** polycondensation; imide saccharin-6-carboxylic acid; disaccharindicarboxylic acid; bisphenol; poly(ester sulfoimide)

## INTRODUCTION

Polyesterimides prepared from diimidedicarboxylic acid with aliphatic fragments are characterized as having fair solubility, thermal plasticity, and melt-forming ability; however, they have low thermal stability.<sup>1</sup> Poly(ester imide) (PEI) prepared from the chlorocarbonylimides of diimidedicarboxylic acid and bisphenol is a highly thermostable polymer.<sup>2</sup> Unlike polyimide, aromatic polysulfimide is easily reprocessed and possesses higher solubility and fire-, thermo-, and radiation stability.<sup>3,4</sup> We have developed a new method of synthesizing sulfodiimidediimide as monomers for the preparation of polysulfoimide.<sup>5</sup> High-temperature polycondensation in a solution and interphase polycondensation at room temperature were found to be the most efficient methods for preparing PEI.

## EXPERIMENTAL

### Synthesis of disaccharindicarboxylic acid

To a solution of 10 g (~0.04 mol) of saccharin-6-carboxylic acid in 40 mL of DMAA were added 6 g of powdered potassium carbonate, 2.86 g (0.02 mol) of  $\beta,\beta'$ -dichlorodiethyl ether, 15 mL of toluene, and ~100

mg of potassium iodide. The reaction mixture was heated at 130°C for 2 h. Then the reaction mixture was cooled to room temperature and poured into 150 mL of distilled water, filtered, and dried in air and then in a vacuum at 60°C–70°C to constant mass. The yield was 6.5 g (68% of theoretical yield). The melting point was 280°C (decomposed).

*N,N*-diethane-1,2-, *N,N*-1,4-dimethylbenzene-, *N,N*-2,5-dimethyl-*p*-xylylene- $\alpha,\alpha'$ -bis(saccharin-6-carboxylic acid) has been analogously synthesized.

### Synthesis of dichlorocarbonylimide of disaccharindicarboxylic acids

Dichlorocarbonylimide from disaccharindicarboxylic acid was synthesized using the method of Zhubanov and Aimbetov<sup>9</sup> with the addition of excess 2.5 molar  $\text{PCl}_5$  and  $\text{POCl}_3$ .

The reaction proceeded at 85°C–90°C for 1.5–2.0 h. At the end of the reaction the excess  $\text{POCl}_3$  was distilled off, and the residue was filtered, washed with dry benzene and chloroform, and further recrystallized from toluene, acetone, and dried in a vacuum at 95°C–100°C. The characteristics of chlorocarbonylimide are presented in Table I.

### Synthesis of poly(ester sulfoimide)

Synthesis of poly(ester sulfoimide) was carried out by polycondensation of dichlorocarbonylimide of disaccharindicarboxylic acid in solution at low and

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TABLE I  
Some Characteristics of Compounds II-V

No.	Compound	Yield (%)	M.p.	Brutto formula	M.W.	Elemental analysis <sup>a</sup>				
						C	H	N	S	Cl
1.	II	80	164	$-_{18}H_{10}O_8N_2S_2Cl_2$	517	41.80	1.93	5.41	12.36	13.70
						42.20	1.91	5.44	13.05	13.50
						42.80	2.49	4.99	11.42	12.63
2.	III	82	146	$-_{20}H_{14}O_9N_2S_2Cl_2$	561	43.00	2.51	5.05	10.88	12.37
						48.51	2.36	4.72	10.7	11.9
						48.28	2.40	4.80	11.0	12.01
3.	IV	84	205	$-_{24}H_{14}O_8N_2S_2Cl_2$	593	50.2	2.89	4.50	10.30	11.40
						50.03	2.93	4.60	10.6	10.80

<sup>a</sup> In denominator—found, in numerator—calculated.

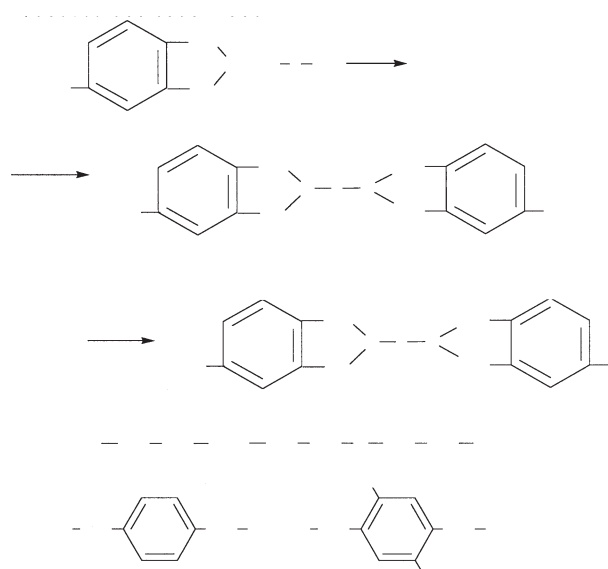
high temperatures. Low-temperature polycondensation was carried out in DMFA and DMAA at 25°C for 2.5 h.

High-temperature polycondensation was carried out in a solution of diphenyloxide in the temperature range of 50°C–180°C for 1–1.5 h. The concentration of the initial components was in the range of 0.4–1.2 mol/L.

First, 2.28 g (0.01 mol) of 2,2-bis(4-hydroxyphenyl)propane, 2.02 g (0.02 mol) of triethylamine, 10 mL of DMAA, and chlorocarbonylimide of *N,N'*-2,5-dimethyl-*p*-xylylene- $\alpha,\alpha'$ -bis(saccharin-6-carboxylic acid) were loaded into a flask. The formed polymer was precipitated with water, filtered, and washed with methanol, and the separated polymer was dried at room temperature in a vacuum.

## RESULTS AND DISCUSSION

The synthesis of poly(ester sulfoimide) (PESI) based on chlorocarbonylimide of disaccharindicarboxylic



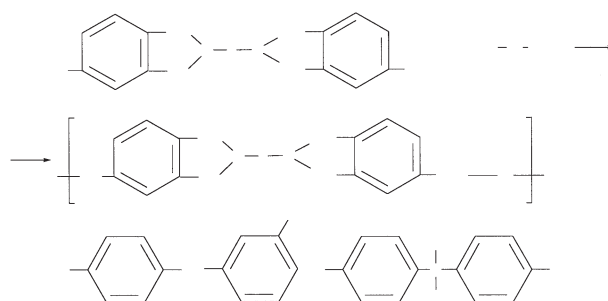
Scheme 1

acid and bisphenol is described below. Chlorocarbonylimide of disaccharindicarboxylic acid III(a–d) was synthesized by the interaction of imide of saccharin-6-carboxylic acid (I) with alkyl- and alkylaryl bishalogenide II(a–d), as shown in Scheme I.

The composition and structure of the compounds were confirmed by data from elemental analysis (Table I) and IR spectroscopy. Absorption bands in the IR spectra of compounds IV(a–d) were found at 1740–1680  $cm^{-1}$ , characteristic of the carboxyl group of the saccharin cycle; 1365–1180  $cm^{-1}$ , characteristic of the  $SO_2$ -sulfoamide group; 3600–3400  $cm^{-1}$ , for the hydroxyl group of carboxylic acids; 1730, 1780, and 725  $cm^{-1}$ , correspond to the imide groups; 740–720  $cm^{-1}$ , for the methylene group in a fragment of diethyl ether; and 870–855  $cm^{-1}$ , corresponding to the 1,2,4,5-substituted benzene ring.<sup>6</sup>

Chlorocarbonylimide of disaccharindicarboxylic acid was synthesized from disaccharindicarboxylic acid by the interaction of phosphorus pentachloride in the presence of a small quantity of phosphorus chloroxide.<sup>7</sup> Prepared *N,N'*-chlorocarbonyl-bis(saccharin-6-carboxylic acid) was used for the synthesis of poly(ester sulfoimide), in which bisphenol of various structures was used as the esterification agent. The reaction of PESI formation proceeded according to Scheme II and was carried out in solution at low and high temperatures.

It was shown that PESI prepared at room temperature in DMFA and DMAA solutions has a charac-



Scheme 2

teristic viscosity not exceeding 0.2 dL/g. This can be explained by the use of high polar solvents, which enabled the interaction reaction of chlorocarbonylimide of acid with bisphenol at room temperature and at the same time creating favorable conditions for the proceeding of the side reaction competing with the basic process of forming high-molecular-weight polymer. The polar aprotic solvent actively interacted with the chlorocarbonylimide group of the dicarboxylic acid.<sup>8</sup>

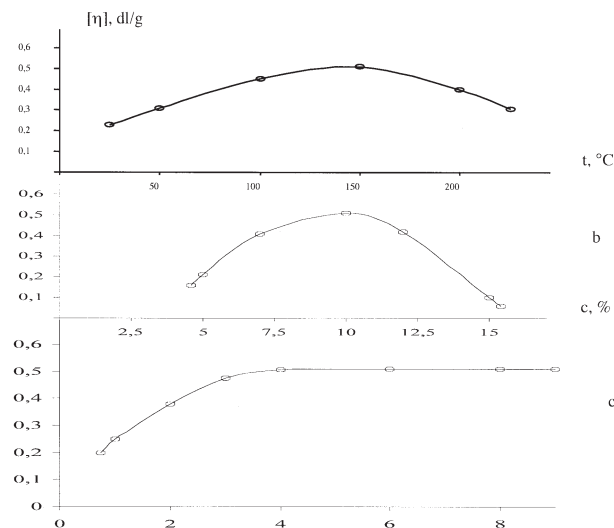
As characteristic viscosity of polymers prepared by low-temperature polycondensation did not exceed 0.2 dL/g, the interaction of chlorocarbonylimide of disaccharindicarboxylic acid with bisphenol at high-temperature polycondensation in solution<sup>9</sup> was studied, using as an example the formation of PESI from chlorocarbonylimides of *N,N'*-diethane-1,2-, *N,N'*-diethyloxy- $\beta,\beta'$ -, *N,N'*-1,4-dimethylbenzene-, and *N,N'*-2,5-dimethyl-*p*-xylylene- $\alpha,\alpha$ -bis(saccharin-6-carboxylic acid).

Polymers with high yields and viscosity were prepared by the interaction of the chlorocarbonylimide *N,N'*-ethane-1,2-bis(saccharin-6-carboxylic acid) [II] with diphenylpropane. Therefore, the effects of the concentration of initial reagents and the duration and temperature of the reaction on the characteristic viscosity of formed PESI was studied, using as an example chlorocarbonylimide [II] and diphenylpropanol.

The best results for the effect of solvent on polycondensation were obtained with diphenyloxy, as in this solvent the initial components were well dissolved and molecular weight of the formed polymer was higher.

When investigating the effect of concentration on the initial substances and temperature and duration of reaction on yield and characteristic viscosity, the optimum conditions for synthesis of PESI were found: concentration of reacting substances, 10–12 wt %; reaction temperature, 120°C–130°C; duration of reaction, 4 h. In these conditions polymer with a characteristic viscosity of 0.60 dL/g was obtained (Fig. 1).

It can be seen from Table II that the viscosity of polymers prepared from chlorocarbonylimide containing aliphatic links was higher than in those containing alkylaromatic and aromatic links, and the melting point of polymers increased when passing from an aliphatic to an aromatic chlorocarbonylimide.



**Figure 1** Dependence of characteristic viscosity of poly(ester sulfoimide) prepared from diphenylpropane and dichlorocarbonylimide of disaccharindicarboxylic acid on: (a) temperature, (b) concentration of initial 2,2-bis(4-hydroxyphenyl)propane, and (c) duration of reaction.

The structure of the polymers was confirmed by IR spectroscopy. Absorption bands at  $1240\text{ cm}^{-1}$  are characteristic of ester bonds and in the range of  $1720\text{--}1780\text{ cm}^{-1}$  of imide bonds.

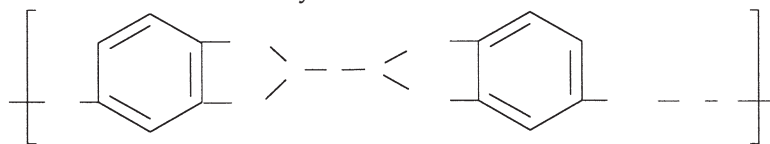
The thermal properties of poly(ester sulfoimide) were studied by the TGA method. From the results, it can be assumed that the thermal stability of the prepared polymers, depending on the structure of the initial components, increased because of the introduction of hydroquinone radicals into polymer links; the temperature at which decomposition of these polymers commenced was in the range of 280°C–340°C; polymers based on diphenylpropane were less thermostable.

PESI does not have a clear melting point.

## CONCLUSIONS

Dichlorocarbonylimide of disaccharindicarboxylic acid was synthesized and characterized. Polysaccharinarylate based on dichlorocarbonylimide and aromatic diol was synthesized at low temperature in solution using the polycondensation method. It was found that the thermal stability of the polymers increased because of the introduction of hydroquinone radicals into polymer links.

TABLE II  
Basic Characteristics of Polysulfoimides of Different General Formulas



No.	-R-	-Ar-	Yield (%)	$\eta_{\log}^a$ (dL/g)	M.p. (°C)	T <sub>commence. of decomp.</sub> (°C)
1.			98	0.6	300	310
2.	—		98	0.55	280	320
3.			95	0.5	260	290
4.			99	0.58	270	300
5.	—		96	0.5	255	310
6.			98	0.45	240	280
7.			98	0.61	310	320
8.	—  —		97	0.58	320	345
9.			96	0.53	295	335
10.			97	0.6	295	310
11.	—  —		95	0.47	315	340
12.			95	0.4	290	300

<sup>a</sup> 0.5 g of polymer in 10 mL of DMAA at 20°C.

Note: TGA of poly(ester sulfoimide) was carried out on heating the samples at a rate of 5°/min.

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