A Novel Synthesis of Aromatic Polyamides from *N,N'*-Isophthaloylbissaccharin and Aromatic Diamines*

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Extension of this reaction to the polycondensation reaction between bifunctional compounds might be expected to give a novel method for preparing polyamides. In this communication, we wish to report a successful synthesis of aromatic polyamides from a new monomer of *N,N'*-isophthaloylbissaccharin and aromatic diamines under mild reaction conditions.

* In this report, we wish to use the common name of "saccharin" instead of "1,2-benzisothiazolin-3-one 1,1-dioxide," for simplicity.

Anal. Calcd for $C_{22}H_{12}N_2O_8S$: C, 52.87; H, 2.44; N, 5.64. Found: C, 52.57; H, 1.91; N, 5.62.

The polycondensation reaction was carried out by the solution polymerization technique in a polar solvent such as dimethylformamide (DMF), DMAc, *N*-methyl-2-pyrrolidone (NMP), and dimethylsulfoxide (DMSO). A typical procedure was as follows: To a solution of 1.000 g (5 mmol) of bis(4-aminophenyl) ether (ODA) in 5 ml of NMP was added 2.482 g (5 mmol) of *N,N'*-isophthaloylbisaccharin at room temperature. The mixture was stirred at that temperature for 24 hr. The resulting viscous solution was poured into 300 ml of hot water. The

Figure 1. Polycondensation of *N,N'*-isophthaloylbissaccharin with ODA in NMP: ●, at 25°C; ○, at 100°C.

Table I. Polycondensation of *N,N'*-isophthaloylbissaccharin with aromatic diamines^a

Diamine	Solvent	Polyamide	
		Yield, %	η_{inh}^b
ODA	NMP	98	1.16
ODA	DMAc	97	0.51
ODA	DMF	95	0.31
ODA	DMSO	99	0.19
MDA	NMP	97	0.45
MPDA	NMP	99	0.21

^a Polycondensation was carried out at room temperature for 24 hr with 5 mmol of the monomers in 5 ml of the solvent.

^b Measured at a concentration of 0.5 g/dl in NMP at 30°C.

precipitated polymer was collected, washed with hot water repeatedly, and dried under vacuum at 60°C. The yield was 1.62 g (98%). The inherent viscosity of the polymer in NMP was 1.16, measured at a concentration of 0.5 g/dl at 30°C. The polymer produced was identified as polyamide by comparing its infrared spectrum with that of the authentic polyamide. The results of the polycondensation with various aromatic diamines including ODA, bis(4-amino-phenyl)methane (MDA), and *m*-phenylenediamine (MPDA) are summarized in Table I. By the

solution polycondensation, polyamides having inherent viscosities up to 1.2 were readily obtained.

Figure 1 shows the rate of polycondensation with ODA in NMP in terms of inherent viscosity of the polymer. The reaction took place fairly rapidly and was almost completed within 5 hr at room temperature to form a high-molecular-weight polyamide. No marked effect of the reaction temperature was observed on the attained molecular weight of the polymer, although the polycondensation was accelerated with rising temperature up to 100°C. The inherent viscosity of the polymer obtained was greatly influenced by the reaction solvents in the following decreasing order: NMP > DMAc > DMF > DMSO.

Although *N,N'*-isophthaloylbissaccharin is apparently less reactive than isophthaloyl chloride,² this monomer can be used to moderate rapid reactions as described above. Moreover, one of the advantages of utilizing the acylsaccharin is that this monomer is a crystalline solid and therefore can be handled more easily than the acyl chloride.

Polyamide formation using activated dicarboxylic acid derivatives such as *N,N'*-isophthaloyldiimidazole³ and *N,N'*-isophthaloyldipyrrolidone⁴ has been reported in recent years. From the results of this investigation and other pub-

lished data, it is presumed that the reactivities of these acid derivatives toward diamines decrease in the following order: the acylimidazolidone > the acylsaccharin » the acylpyrrolidone.

Further study of the polycondensation reaction of the related compounds is in progress.

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