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NEW POLYMER SYNTHESIS: POLYMERS POSSESSING DIIMINOSULFOXIDE FUNCTIONALITY IN THE BACKBONE

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ABSTRACT

Three new monomers with sulfinylimine functionality have been prepared. They react with appropriate aromatic diamines to give a new class of polymers having the diiminosulfoxide ($-\text{NH}-\text{SO}-\text{NH}-$) functional group in their backbone. The monomers as well as polymers are characterized by spectral data and elemental analysis. Experiments were carried out to find the effect of reaction time and solvent on the polymerization reaction. The polymers are soluble in electron-donating organic solvents, such as DMF, NMP, and DMAC, and insoluble in most nonpolar solvents. They are thermostable up to 200°C , but their stability in the presence of sulfuric acid and aqueous sodium hydroxide is low.

INTRODUCTION

The reaction of any isocyanate compound with another compound bearing hydroxyl group under appropriate conditions leads to urethanes. The mechanisms and applications of the reactions have been investigated in great detail [1-7]. However, the sulfinylimine functionality, which is isosteric with the isocyanate group, has not received adequate attention. In principle, analogously to isocyanate, sulfinylimine should react with any reactive nucleophile (NuH) to generate the new functionality

sure. The monomers were crystallized, and the polymers were purified by reprecipitation for characterization.

General Method of Monomer Synthesis

The diamine (0.005 mol) was placed in a 250-mL round-bottom flask fitted with reflux condenser and dropping funnel. Then thionyl chloride (100 mL) was added slowly over a period of 1/2 h while keeping the temperature of the reaction mixture at 5–10°C. After that, the reaction mixture was refluxed for 4 h, during which time the almost colorless solution turned yellow. Removal of the excess thionyl chloride by rotary evaporator, followed by crystallization from methylene chloride–hexane, gave the desired monomers, which are homogeneous as judged by TLC. Attempted purification of the monomers by flash column chromatography resulted in extensive decomposition.

General Method of Polymer Synthesis

Crystallized monomer **2** (0.02 mol) was dissolved in DMF, DMSO, DMAC, or NMP (500 mL) and stirred under nitrogen. Amine **3** (0.02 mol) was taken in the same solvent (150 mL) and was added slowly to the well-stirred reaction mixture at room temperature over 3/4 h. During the addition, the color of the reaction mixture changed from yellow to orange. The reaction was heated on an oil bath at 120°C. After 8 h of heating the dark colored solution was poured into a large excess of ice water. The black mass which precipitated out was filtered and dried to give the desired polymers. The polymers were purified by reprecipitation from DMF–ether and characterized by spectroscopy and elemental analysis.

RESULTS AND DISCUSSION

Monomers

The reaction of aromatic diamines with an excess of thionyl chloride at 80°C gave the desired monomers in quantitative yield. The monomers are highly sensitive to moisture and any protic solvent but are stable under nitrogen and at low temperature (10°C), consistent with our earlier fin-

TABLE 1. Physical Characteristics and Yield of the Monomers OSN-R-NSO

Monomer	R	Color	Yield, %	mp, °C
2a	-Ph-O-Ph-	Yellow	92	144
2b	-Ph-CH ₂ -Ph-	Yellow	98	121
2c	-Ph-Ph-	Yellow	95	129

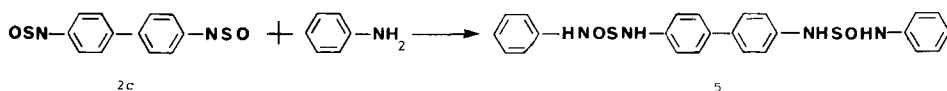
dings [9, 10]. The physical properties of the monomers are given in Table 1.

The monomers were characterized by spectral as well as elemental analysis. Monomer **2a** in chloroform solution shows two IR bands, at 1350 and 1235 cm^{-1} , which are assigned to asymmetric and symmetric stretching vibrations of S=O. Similarly, Monomers **2b** and **2c** possess IR bands at 1355, 1230 cm^{-1} and 1357, 1220 cm^{-1} , respectively. A band near 1601 cm^{-1} in all the monomers is characteristic of the phenyl group. The ^1H NMR of Monomer **2c** in CDCl_3 exhibits an A_2B_2 type of spectrum for four aromatic protons at 6.8 to 7.15 ppm, and other aromatic protons appear at 7.6 ppm. Proton-decoupled ^{13}C NMR of Monomer **2c** shows three signals at 126 to 151 ppm. Similar types of ^1H NMR and proton noise-decoupled ^{13}C NMR were obtained for Monomers **2a** and **2c**.

Polycondensation

To investigate the general scope of the polycondensation reaction of disulfinylimine monomer with various diamines and to identify the structure of the product, a model reaction was carried out. This is represented in Scheme 2.

Thus, Monomer **2c** upon heating with two molar equivalents of aniline in DMF under nitrogen resulted in the formation of Compound **5** in 83% yield. The chemical structure of this compound was confirmed by spectroscopy and elemental analysis. Four protons due to two $-\text{NH}-\text{SO}-\text{NH}-$ groups were observed by NMR at 6.9 ppm, and addition of



Scheme 2. Model reaction of Monomer **2c** with aniline.

D₂O resulted in their disappearance, confirming the assignment. Electron-impact ionization mass spectroscopy (EIIMS) also confirmed the structure of Compound 5.

The prepared monomers were reacted with the diamines in a 1:1 molar ratio to give the target polymers in varying yields. The IR spectra of the newly synthesized polymers (in a Nujol mull) exhibit a broad band in the region of 3400 cm⁻¹ and comparatively sharp bands around 1350 and 1215 cm⁻¹. The former is due to -NH- stretching and the latter two are characteristics of asymmetric and symmetric S=O stretching. All the polymers possess a broad band near 1602 cm⁻¹, which is indicative of aromatic groups. The elemental analyses also confirmed the structure of the polymers (see Table 2).

One of the interesting aspects of this new polycondensation reaction is its strongly solvent-dependent nature, which has been investigated in detail. Thus, polar solvents like DMAC, DMF, NMP, and DMSO serve as the best reaction media, whereas nonpolar, solvents like benzene and toluene fail to give any polymer. In most of the cases, a complex mixture of the condensation product of one to three molecules of silfinylimine monomer and one to three molecules of amine were isolated in poor yield, along with hydrolyzation products of the monomers. The compositions of the products were confirmed from their molecular weight obtained by

TABLE 2. Elemental Analysis of the Polymers^a

Polymer	R	R ₁	% C		% H		% S	
			Calc	Found	Calc	Found	Calc	Found
4a	DPE	Ph	54.00	53.90	4.0	3.91	16.00	15.88
4b	DPE	DPH	60.50	60.31	4.2	4.11	13.44	13.29
4c	DPE	DPM	61.22	61.35	4.48	4.32	13.06	12.87
4d	DPM	Ph	57.28	57.09	4.52	4.29	16.08	15.91
4e	DPM	DPH	63.29	63.17	4.64	4.58	13.50	13.36
4f	DPM	DPM	63.93	63.75	4.91	4.83	13.11	12.95
4g	DPH	Ph	56.25	56.12	4.16	4.07	16.66	16.50
4h	DPH	DPH	62.60	62.49	4.34	4.26	13.91	13.77
4i	DPH	DPM	63.29	63.21	4.64	4.49	13.50	13.41

^aPh = Phenyl, DPH = -Ph-Ph-, DPM = -PH-CH₂-Ph-, DPE = -Ph-O-Ph-.

TABLE 3. Influence of Polycondensation Solvent on Yield and Inherent Viscosity of Polymers

Polymer	Solvent	Yield, %	Inherent viscosity, ^a dL/g
4a	NMP	78	0.19
4a	DMF	52	0.15
4a	DMAC	71	0.13
4a	Benzene	0	
4b	NMP	68	0.25
4b	DMF	55	0.14
4b	Benzene	0	
4c	NMP	69	0.15
4c	Benzene	0	
4d	DMF	63	0.12
4d	Toluene	0	
4e	DMAC	57	0.16
4e	Benzene	0	
4f	NMP	73	0.27
4f	Benzene	0	
4g	DMF	60	0.12
4g	Toluene	0	
4h	DMSO	66	0.11
4h	Toluene	0	
4i	NMP	75	0.13
4i	Toluene		

^aMeasured at a concentration of 0.05 g/dL in DMF at 30°C.

EIIMS and elemental analysis. The influence of solvents on yield and inherent viscosities is given in Table 3.

The inherent viscosities of the polymers in NMP are low. We initially thought this could be due to a specific solvent effect. However, the inherent viscosities of Polymers **4a**, **4d**, and **4g** in DMF, DMAC, and DMSO under the same conditions were found to be very close to those in NMP. Presumably, the starting monomers react with trace amount of moisture present in the solvent, which leads to undesirable by-products and low molecular weight polymers. Besides, a (2+2) cycloaddition reaction of two sulfinylimine monomers either in a regiospecific or a nonregiospecific way might be a competing reaction which could also lower the viscosity.

The effect of reaction time on the yield of a representative example is shown in Fig. 1. In general, the maximum yield occurred after 8 h of reaction.

Characterization

All the polymers are black in color and soluble in most polar solvents and insoluble in common nonpolar organic solvents (see Table 4).

The polymers were found to be unstable under either acidic or basic conditions, i.e., treatment of the polymers with either concentrated sulfuric acid or 10% sodium hydroxide resulted in almost complete decomposition in 50 h (see Fig. 2).

We expected the prepared polymers not to be thermally stable due to the presence of the relatively thermolabile $-\text{NH}-\text{SO}-\text{NH}-$ group in the backbone. However, they are found by TGA to be stable up to 200°C in air. The initial weight loss of 4% at 100°C is probably due to loss of entrapped solvents. The maximum weight loss takes place at $200-400^{\circ}\text{C}$ (see Fig. 3). Results of isothermal aging of the polymers in air and in nitrogen

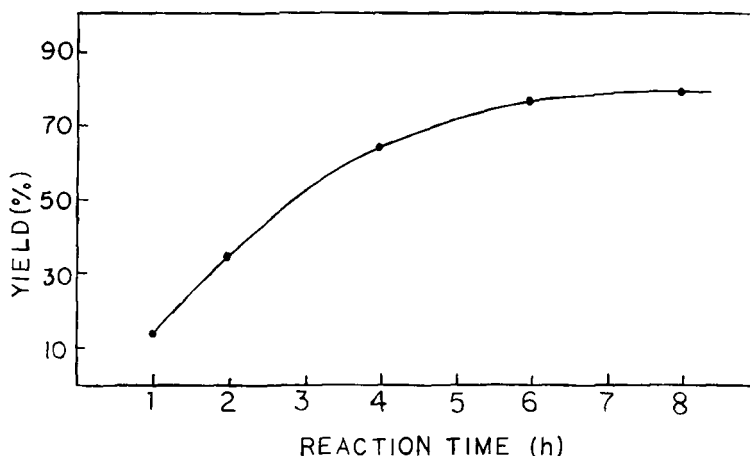


FIG. 1. Effect of reaction time on yield of Polymer 4a.

TABLE 4. Solubility Characteristics of the Prepared Polymers^a

Polymer	DMF	DMAC	DMSO	NMP	THF	EA	FA	MEK	BZ	CH
4a	+	+	+	+	+ -	+ -	+	+ -	-	-
4b	+	+	+	+	+ -	+ -	+	+ -	-	-
4c	+	+	+	+	+ -	+ -	+	+	-	-
4d	+	+	+	+	-	-	+	+ -	-	-
4e	+	+	+	+	+ -	-	+	+ -	-	-
4f	+	+	+	+	+ -	+ -	+	+ -	-	-
4g	+	+	+	+	-	-	+	+	-	-
4h	+	+	+	+	-	-	+	+ -	-	-
4i	+	+	+	+	-	-	+	+	-	-

^a(+) Soluble, (+-) partially soluble, (-) insoluble. Abbreviations: EA, ethyl acetate; FA, formic acid; BZ, benzene; CH, chloroform.

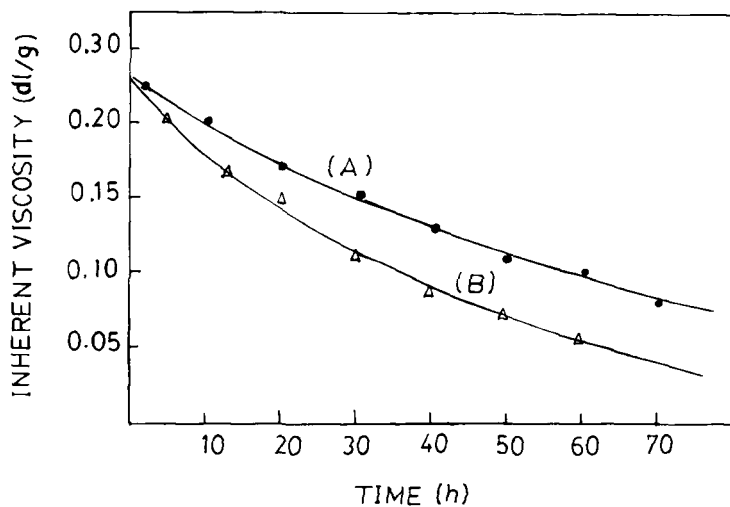


FIG. 2. Stability of Polymer 4i in (A) 2% aqueous sodium hydroxide and (B) concentrated sulfuric acid.

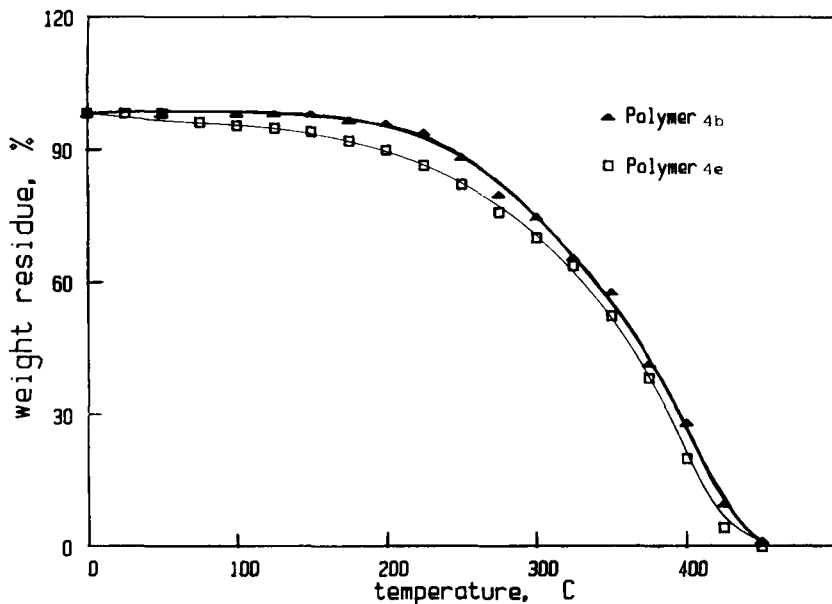


FIG. 3. Thermogravimetric (TGA) curve of Polymers **4b** and **4e** in air (5°C/min).

are given in Table 5. The results show the polymers are thermally more stable in nitrogen than in air at elevated temperature.

CONCLUSIONS

1. Disulfinylimine compounds could serve well as one component in polycondensation reactions. These compounds can be prepared easily and may be stored for a short period of time at low temperature and under inert atmosphere.

2. The condensation reaction of disulfinylimine and diamine leads to low molecular weight polymers at 55 to 78% yield.

3. The polymers are not stable to acidic or alkaline conditions. They are, however, thermally stable up to 200°C without substantial degradation.

TABLE 5. Weight Loss (in %) on Isothermal Aging at 200°C

	Polymer	Aging time, h				
		1	2	4	8	16
In nitrogen	4a	0.9	1.3	1.7	2.9	6.5
	4b	0.6	1.5	1.9	3.8	7.1
	4e	0.1	1.3	1.6	2.7	5.9
	4g	0.4	1.1	1.9	2.5	6.1
	4i	0.7	1.9	2.6	3.9	8.3
In air	4a	1.3	2.5	3.3	6.1	8.9
	4b	1.6	2.2	3.0	6.7	9.7
	4e	1.1	2.5	3.1	5.9	9.2
	4g	0.9	2.1	3.0	5.2	7.7
	4i	1.3	2.4	3.8	6.0	9.1

Continuing study is directed at increasing the viscosity of the polymers. The reactions of other nucleophiles with disulfinylimine monomers are also under investigation.

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