Table IV
Basic Properties of Diamines and Some Intermediates

Compound	Cyclizn Condn (°C/hr)	Recrystallization from[a]	Yield (%)	Mp (°C)	General Formula	Anal. Found (%)			Anal. Calcd (%)		
						C	H	N	C	H	N
IIIa		DMF	90	230 dec	$C_{22}H_{18}N_8O_6$	53.60	3.62	22.54	53.88	3.67	22.83
IIIb		DMF–H_2O (1:1)	92	245 dec	$C_{22}H_{18}N_8O_6$	53.70	3.59	22.48	53.88	3.67	22.83
IIIc		Ethanol	88	199–200 dec	$C_{21}H_{17}N_9O_6$	50.98	3.38	25.63	51.40	3.46	25.66
IVa	260/3	Alcohol-water (1:1)	78.5	246–247	$C_{22}H_{14}N_8O_4$	59.33	2.84	24.33	58.15	3.07	24.67
IVb	260/3	Acetone-water (1:1)	80	313–315	$C_{22}H_{14}N_8O_4$	57.72	2.90	24.65	58.15	3.07	24.67
IVc	210/4	Acetone-water (1:4)	90	315	$C_{21}H_{13}N_9O_4$	55.15	2.40	27.35	55.40	2.42	27.70
Va		Dioxane-water (1:1)	70	318–320	$C_{22}H_{18}N_8$	66.02	4.94	27.90	66.62	4.63	28.35
Vb		DMF–H_2O (1:2)	75	330–331	$C_{22}H_{18}N_8$	66.84	4.52	28.04	66.62	4.63	28.35
Vc		Ethanol	70	338–340[b]	$C_{21}H_{17}N_9$	63.45	3.87	31.63	63.81	4.05	31.90

[a] See Table I, footnote *b*. [b] Lit. mp 338° (see ref 3, 14, and 13).

temperature for 6–8 hr. The resulting solution was poured into distilled water. The polymer was thoroughly washed with water, extracted with ethanol for 45–50 hr, and dried under reduced pressure, to a constant weight at 50–60°. The general properties and characteristics of poly(*o*-amido triazoles) are given in Table II.

Poly(triazoloquinazolines) were prepared by solid-state cyclodehydration of aromatic poly(*o*-amido triazoles) under reduced pressure (0.5–1 mm Hg) at 50, 100, 150, 200, 250, and 300° for 1 hr and at 350–375° for 12 hr.

The basic characteristics of poly(triazoloquinazolines) (XV–XXXIX) are given in Table III.

Synthesis of Polymers in P_n. Bis[5-(2-aminophenyl-1,2,4-triazol-3-yl]arylene (0.01 mol), the dinitrile (0.01 mol) of aromatic dicarboxylic acid, and P_n (20 g) were placed into a three-necked flask. The mixture was stirred at 100, 150, and 200° for 1 hr and at 250° for 3 hr. The resulting polymers are soluble only in H_2SO_4; η_{red} is 0.2–1.2.

Investigations of Polymers. The curves of the dynamic thermogravimetric, differential thermal, and differential thermogravimetric analyses were obtained on the derivatograph of the "Paulik, Paulik and Erdel" type in air. The temperature increase rate is 4.5°/min.

The ir spectra of polymers and model compounds were taken with the UR-10 and UR-20 spectrophotometers by using powders pressed with KBr.

The uv spectra of polymers and model compounds were taken with the Hitachi spectrophotometer.

Polymerization of 4-Hydroxybenzenesulfonyl Chloride

R. W. Campbell* and H. Wayne Hill, Jr.

Phillips Petroleum Company, Bartlesville, Oklahoma 74004. *Received April 2, 1973*

ABSTRACT: The conversion of 4-hydroxybenzenesulfonyl chloride (I) to high molecular weight poly(1,4-phenylenesulfonate) by treatment with tertiary amines in polar amide solvents is described. Conditions giving the highest molecular weight polymer are 1.25 equiv of triethylamine in hexamethylphosphoramide at 0°. This crystalline polymer has a glass transition temperature of 119° and a crystalline melting temperature of 276°. Solution polymerization of 3,5-dimethyl-4-hydroxybenzenesulfonyl chloride (II) is also described, along with copolymerization of I and II. Melt polymerization of I produces a polymer containing both sulfonate and hydroxysulfone repeat units.

There has been considerable interest shown in polymers of the general type $(-C_6H_5X-)_n$ throughout the last decade due largely to their high melting points and thermal stability. Several members of this "poly(phenylene) family" have recently become commercial products (X = S, CO_2, CONH). Synthesis of poly(1,4-phenylenesulfonate)($PPSO_3$, X = SO_3) has been prevented by the lack of a suitable monomer (*e.g.*, 4-hydroxybenzenesulfonyl chloride, I). Although a variety of 3,5-disubsituted-4-hydroxybenzenesulfonyl chlorides have been reported,[1-4] the parent compound was only recently isolated.[5,6] We found that I can be prepared by treating sodium 4-hydroxybenzenesulfonate with an excess of thionyl chloride in the presence of a catalytic amount of dimethylformamide at 60°. This study is concerned with the conversion of I into a high molecular weight polymer. Low-temperature solution polymerizations conducted in polar amide solvents in the presence of tertiary amines were found to be quite suitable for this reaction.

Results and Discussion

Polymer Properties. Poly(1,4-phenylenesulfonate) is normally obtained as a white, powdery solid which is insoluble in common organic solvents as well as most polymer solvents [*e.g.*, methylene chloride, tetrahydrofuran (H_4furan), acetone, dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), tetramethylurea (TMU), sulfolane, formic acid, etc.] Polymer of intermediate molecular weight (inherent viscosity, ≤0.5) is soluble in dimeth-

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Table I
Effect of Solvent on Polymerization of 4-Hydroxybenzenesulfonyl Chloride[a]

Solvent	η_{inh}[b]	E[c]
HMP	0.72 (H)	30
TMU	0.47 (H)	23.1
NMP	0.10 (N)	32.2
DMAC	0.10 (N)	37.8
DMF	0.07 (N)	36.7
Sulfolane	0.06 (N)	44
Cyclohexanone	0.06 (N)	18.3
CH_2Cl_2	0.02 (N)	9.0
H_4furan	0.02 (N)	7.6

[a] Polymerizations carried out at 25° using 1.5 equiv of triethylamine. [b] Inherent viscosity measured as 0.5% solutions at 30° in HMP (H) or NMP containing 4% LiCl (N). [c] Literature dielectric constant at 20-30°.

Table II
Effect of Base on Polymerization of 4-Hydroxybenzenesulfonyl Chloride[a]

Base	η_{inh}[b]
Triethylamine	0.10
Tri-*n*-butylamine	0.08
Triisopropylamine	0.08
Triethylenediamine	0.06
Pyridine	No polymer
2,4,6-Trimethylpyridine	0.13
$Ca(OH)_2$	0.24
CaO	0.19

[a] Polymerizations carried out at 25° in NMP using 1.5 equiv of base. [b] Inherent viscosities measured as 0.5% solutions at 30° in NMP containing 4% LiCl.

ylacetamide (DMAC) (0.5%), TMU (0.5%), and NMP (10-15%) when 4% lithium chloride is added to these solvents. All molecular weights are soluble in hexamethylphosphoramide (HMP) up to about 15% solids. $PPSO_3$ is a crystalline polymer having a crystalline melting temperature, T_m, of 276° and a glass transition temperature, T_g, of 119°. Thermal stability of this aromatic polymer was investigated by TGA. In programmed runs (10°/min), 5% weight loss was observed at 375°. A rapid, exothermic weight loss then occurs with phenol, sulfur dioxide, and triethylamine (used as a base in the polymerization reaction) detected as volatile by-products. Substantial char is produced, resulting in 52% weight retention at 585°. Both the temperature at which massive decomposition occurs and the rate of weight loss at a temperature suitable for melt fabrication (0.064-0.003%/min at 290°) were found to be more dependent on molecular weight than any other variable examined (*e.g.*, end capping or method of isolating polymer). Solubility characteristics of $PPSO_3$ have prevented precise molecular weight measurements; however, the results of polymerizations involving known amounts of a monofunctional reactant indicate a $\bar{M}_n$ of about 30,000 for polymer having η_{inh} of 1.0. This polymer can be pressed into film at 280-290°. Quenching yields clear, rigid samples which show no crystallinity by X-ray diffraction. Film or fibers pulled from the melt can be drawn at 135° to give strong, tough specimens. Crystallinity can be developed by annealing at 185°.

All samples contain an acetone soluble fraction (~10-15%) which has a η_{inh} of 0.04-0.06. The absence of end groups (spectrally and by elemental analysis) in this low molecular weight material is an indication that they are cyclic oligomers. Numerous reports of this type of product from condensation polymerizations have appeared.[3,7,8]

Solution Polymerization of I. Interfacial polymerization is the technique used most frequently in the past to prepare poly(arylsulfonates).[9-11] This has obvious disadvantages when applied to a hydroxybenzenesulfonyl chloride and, in fact, yielded no polymer when attempted. Hall has reported[12] that the polymerization of 3,5-dimethyl-4-hydroxybenzenesulfonyl chloride is best accomplished by treating a nitrobenzene solution of the sulfonyl chloride with triethylenediamine. Under these conditions, however, I yielded only low molecular weight polymer (η_{inh} = 0.06).

The results of a number of polymerizations carried out in various solvents are summarized in Table I. These reactions involved the addition of 1.5 equiv of triethylamine to a solution of I and subsequent stirring of the reaction mixture at 25° for 5 min to 2 hr. The yields of polymer in this and succeeding tables do not vary significantly (75-85%) except when very low molecular weight polymer was obtained ($\eta_{\text{inh}} < 0.05$). The molecular weight was found to be highly dependent on the choice of solvent. A high dielectric constant coupled with the ability to dissolve $PPSO_3$ are requirements for a successful polymerization. HMP, previously mentioned as the best solvent for $PPSO_3$, was also found to be the preferred solvent for its preparation.

The results of a group of polymerizations carried out in NMP at 25° and involving various bases are summarized in Table II. Triethylamine gave better results than the other aliphatic tertiary amines examined. While pyridine gave no polymer, the more strongly basic 2,4,6-trimethylpyridine gave somewhat higher molecular weight polymer than triethylamine. Slurries of CaO and $Ca(OH)_2$ could also be used to prepare $PPSO_3$.

A major factor in obtaining increased molecular weight was found to be a low reaction temperature. The freezing point of the solvents employed was the limiting feature in examining this variable. Results of a number of low temperature polymerizations are shown in Table III. The superiority of HMP as a polymerization solvent was again observed and outweighed the effect of lower temperature possible when other solvents were used.

DMF has a much lower freezing point than the other amide solvents; however, it is not as good a solvent for this polymerization. Polymer having $\eta_{\text{inh}} \cong 0.3$ was produced from 0 to −40°. At −60°, only a trace of low molecular weight $PPSO_3$ was obtained.

The importance of solvent polarity is further illustrated by the fact that no polymer was obtained from H_4furan at −35° using triethylamine.

At these low temperatures, triethylamine was clearly the preferred base, giving higher molecular weight product than other tertiary aliphatic amines examined. Using 1.25 equiv of this amine in HMP, polymer with a η_{inh} of ~1.0 can be prepared. Trimethylpyridine and $Ca(OH)_2$, bases which gave somewhat better polymer than triethylamine at 25°, yielded no polymer at −35° in an NMP-DMAC (60:40) mixture. However, polymer was produced when $Ca(OH)_2$ was employed at 0°.

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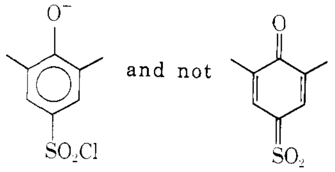
Table III
Low-Temperature Polymerization of 4-Hydroxybenzenesulfonyl Chloride[a]

Solvent	Temp (°C)	η_{inh}[b]
NMP	−30	0.41 (N)
NMP-DMAC (60:40)	−38	0.62 (H)
NMP-DMAC-HMP (50:30:20)	−45	0.84 (H)
HMP-NMP (80:20)	−20	0.88 (H)
HMP	0	0.89 (H)

[a] Polymerizations carried out using 1.5 equiv of triethylamine. [b] Inherent viscosities measured as 0.5% solution at 30° in NMP containing 4% LiCl (N) or in HMP (H).

The concentration of I was varied in these polymerizations from 3-25% (g/100 g of solvent), with some improvement in molecular weight observed as the concentration approached 20% (approximately 1 *M*). Reaction time did not appear to have an effect on molecular weight in the range examined (5 min to 16 hr). The rate of addition of the base and the method of work-up (*e.g.*, nonaqueous precipitation and pH of the precipitating media) also had no significant effect on molecular weight of the polymer produced.

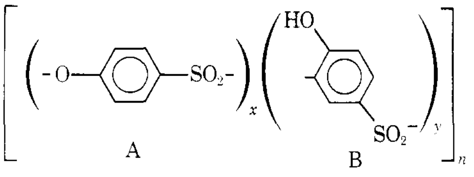
In all reactions giving rise to $PPSO_3$, a bright yellow color is produced when the base and sulfonyl chloride are mixed. This color disappears when the polymerization is complete. Similar observations were made by Hall concerning the interaction of 3,5-disubstituted-4-hydroxybenzenesulfonyl chlorides and triethylenediamine. He concluded from trapping experiments and titrations that the colored species (λ_{max} 310-330 mμ) were the phenolate anions rather than "quinoid sulfene" intermediates. In polymerization reactions of I, the anion is apparently unreactive in H_4furan at −35° and DMF at −60° and not produced when bases other than aliphatic tertiary amines are used at low temperatures.

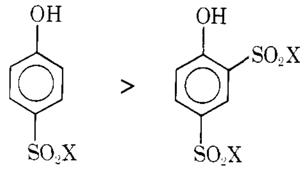


Copolymerization of I with 3,5-Dimethyl-4-hydroxybenzenesulfonyl Chloride (II). Hall has reported[12] the preparation of polymer from II, with triethylenediamine in nitrobenzene as the preferred conditions (η_{inh} = 0.57). The poor polymerization behavior of I under these conditions (η_{inh} = 0.06), due to a lack of polymer solubility, combined with the fact that II gave low molecular weight polymer (η_{inh} = 0.30) in a 60:40 NMP-DMAC mixture with triethylamine at −37° made the preparation of high molecular weight copolymers from I and II seem unlikely. However, HMP was found to be a remarkably good solvent for polymerizing II in the presence of triethylamine (η_{inh} = 0.79). The results of a series of copolymerizations carried out in HMP at 0° using 1.5 equiv of triethylamine are shown in Table IV. No crystallinity was observed by dta in premelted and quenched samples of homopolymer from II and copolymers from I and II. The existence of a low degree of order, approaching crystallinity, was indicated by the polymer melt temperatures[13] of the homopolymer from II and the copolymer from a 75-25 mol % mixture of I and II. Values for these materials were found to be 100-125° higher than T_g, as compared with the 40-60° difference normally encountered with amorphous polymers.

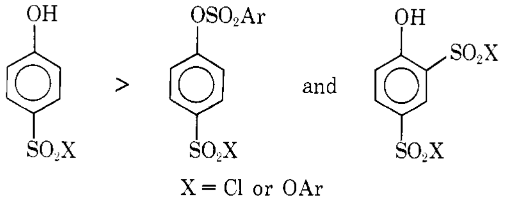
An attempt was made to prepare copolymers of I with bisphenols and disulfonyl chlorides (*e.g.*, 2,2-bis(*p*-hydroxyphenyl)propane and bis(4-chlorosulfonylphenyl) ether. These monomers, however, did not polymerize readily in HMP with triethylamine (η_{inh} = 0.08). Their presence at the 5 mol % level in a reaction of I with triethylamine at 0° gave a low molecular weight product (η_{inh} = 0.17).

Melt Polymerization of I. The preparation of sulfonate esters from a sulfonic acid and an alcohol is not a good synthetic procedure. As might be expected, heating 4-hydroxybenzenesulfonic acid to 235° over a 3-hr period yielded a badly degraded reaction mixture with no evidence of polymer formation. The reaction mixture was entirely water soluble. When I was heated slowly to 275° over a 5-hr period at reduced pressure with a N_2 sweep, considerable HCl was evolved and the reaction mixture appeared as a viscous liquid at this temperature. Upon cooling to room temperature under N_2, the product was an amber, transparent solid (82% yield, T_g = 148°, polymer melt temperature 215°) having an inherent viscosity of 0.33 in NMP. It could not be precipitated from NMP with water and was soluble in acetone. Spectral data (hydrogen bonded OH in the ir, uncoupled aromatic proton at 8.04 in the nmr) indicated the product to be a copolymer containing approximately 60% of the hydroxysulfone structure (B) resulting from sulfonylation of the aromatic ring. Although branching may occur to a limited extent, the following trends in reactivity should tend to minimize it





in nucleophilicity



in propensity of ring for electrophilic substitution. The net result of these trends is that nucleophilic attack by phenolic groups present on the polymer chain and electrophilic substitution of aromatic rings in the polymer chain, both of which are branch forming reactions, are minimized. The results of similar reactions indicated that traces of residual DMF catalyze this melt polymerization.

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Table IV
Copolymerization of 4-Hydroxybenzenesulfonyl Chloride (I) and 3,5-Dimethyl-4-hydroxybenzenesulfonyl Chloride(II)

Mol % I	η_{inh}[b]	T_g (°C)	T_m (°C)[c]
100	0.76	117	277
75	0.76	130	(255)
50	0.74	135	(180)
25	0.71	148	(190)
0	0.79	153	(250)

[a] Polymerizations carried out in HMP at 0° using 1.5 equiv of triethylamine. [b] Inherent viscosities measured as 0.5% solutions in HMP at 30°. [c] Values shown in parentheses are polymer melt temperatures, determined on a bar with a temperature gradient, for polymers which show no melting by dta.

Experimental Section

Reagents and Monomers. 4-Hydroxybenzenesulfonyl chloride (I) was prepared from the reaction of sodium 4-hydroxybenzenesulfonate with thionyl chloride in the presence of a catalytic amount of DMF carried out at 60°.[5] Sodium 3,5-dimethyl-4-hydroxybenzenesulfonate was prepared from 2,6-dimethylphenol according to the method of Karrer and Leiser[14] using sulfuric acid monohydrate at 100-110°. 3,5-Dimethyl-4-hydroxybenzenesulfonyl chloride (II) was prepared from the sulfonate salt by treatment with thionyl chloride in DMF solvent.[3] The tertiary amines were distilled from potassium hydroxide and stored under nitrogen over potassium hydroxide. Solvents were purified in the usual manner and stored under nitrogen.

Solution Polymerization. The reactions were carried out in a dry environment under N_2 with stirring. The base was usually added to a solution of the sulfonyl chloride. A nonsolvent for the polymer was added after the reaction was complete and the products were thoroughly washed and dried.

Poly(1,4-phenylenesulfonate). To a stirred solution of 1.93 g (10 mmol) of I in 10 ml of HMP under a nitrogen atmosphere was quickly added 1.26 g (12.5 mmol) of triethylamine at 0°. A bright yellow color was produced immediately which faded in 30 sec as the solution became viscous. After stirring 6 min at 0°, the polymer was precipitated by the addition of 200 ml of water with vigorous stirring. The polymer was collected by filtration and washed on the filter with 200 ml of water and 200 ml of methanol. It was washed by stirring thoroughly in water (300 ml), methanol (3 × 200 ml) and refluxing acetone (2 × 200 ml). After drying in a vacuum oven at 70°, 1.29 g (83%) of white polymer was obtained, inherent viscosity 0.97 (0.5 g/dl of HMP solution at 30°).

Anal. Calcd for $C_6H_4O_3S$: C, 46.1; H, 2.6; S, 20.5. Found: C, 46.0; H, 2.7; S, 20.5.

Melt Polymerization of I. In a small glass reactor was placed 5.5 g (28.6 mmol) of I. Air was removed by alternately pressuring with nitrogen (10 psig) and evacuating. The system was heated at 90-100° for 2 hr with nitrogen being bubbled through the melt and the pressure maintained at 3.5 mm of Hg. After heating 2 additional hr at 100-160°, the reaction mixture solidified. At 250° it remelted and the dark, viscous liquid was heated at 250-275° for one hour. The system was cooled to room temperature under N_2, yielding 3.6 g (82%) of a glassy solid which showed no crystallinity by DTA, inherent viscosity 0.33 (0.5 g/dl of NMP solution at 30°): ir (film) 2.9-4.0 μ (OH), 7.3 and 8.6 μ (SO_2); nmr ($CDCl_3$) δ 7.12 (s, OH), 7.40 (d, J = 9 Hz, protons ortho to OH), 7.8-8.4 (m, protons ortho to SO_2).

Isomerization Polymerization of 1,3-Oxazine. I. Polymerization of Unsubstituted 5,6-Dihydro-4*H*-1,3-oxazine Giving Poly(*N*-formyltrimethylenimine) and Its Alkaline Hydrolysis to Poly(trimethylenimine)

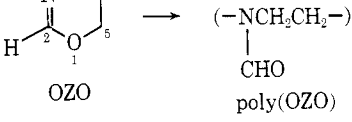
Takeo Saegusa,* Yoshitomi Nagura, and Shiro Kobayashi

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan.

Received December 19, 1972

ABSTRACT: Unsubstituted 5,6-dihydro-4*H*-1,3-oxazine (OZI) is synthesized for the first time by the reaction of 3-aminopropanol with *tert*-butyl isocyanide catalyzed by AgCN. OZI was found to polymerize by various cationic initiators such as dimethyl sulfate, concentrated H_2SO_4, boron trifluoride etherate, ethyl trifluoromethanesulfonate, methyl tosylate, and methyl iodide. The polymer structure of poly(*N*-formyltrimethylenimine) (poly(OZI)) was established by ir and nmr spectra. The polymer was a white solid, melting point about 120°, which is soluble in water at room temperature and in polar solvents such as dimethylformamide, acetonitrile and methanol when warmed up. The solid polymer was shown to be partially crystalline by X-ray diffraction analysis. The alkaline hydrolysis of poly(OZI) gave slightly crystalline linear poly(trimethylenimine). This is the first time the linear poly(trimethylenimine) has been prepared.

Recently, we have reported for the first time the isomerization polymerization of unsubstituted 2-oxazoline (OZO), a five-member cyclic imino ether to give poly(*N*-formylethylenimine) (poly(OZO)) (eq 1).[1-4] The alkaline hydrolysis of the polymer has provided a new synthetic method of preparing poly(ethylenimine) with no branching.[3] These interesting new findings prompted us to examine the polymerization of 5,6-dihydro-4*H*-1,3-oxazine (OZI). Although several 2-substituted oxazines have been polymerized at elevated temperatures by cationic initiators to polymers having the structure of poly(*N*-acyltrimethylenimine),[5] the polymerization of unsubstituted 1,3-oxazine has not been reported so far, and even the OZI



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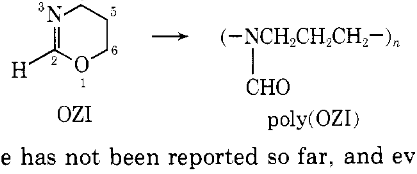

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