by-pass. A stirring bar magnet was placed in the liquid and 2.80 ml (0.02 mol) of distilled triethylamine was added from a graduated pipet. A clear solution formed. Sebacyl chloride (2.13 ml, 0.01 mol) was dissolved in 15 ml of 1,2-dichloroethane in the addition funnel and the assembly was then set in a small ice–water bath on a magnetic stirrer. While the phenol solution was stirred at medium speed, the acid chloride solution was dripped in over a period of about 40 min. The solution became moderately viscous and a precipitate of triethylamine hydrochloride formed. About 5 ml of solvent was used to rinse in residual acid chloride from the funnel. After 1 hr of reaction time the polymer was precipitated by pouring into hexane (250 ml) and was collected, washed, and dried as in preceding preparations.

The yield was 95% and the inherent viscosity was 0.73. Other solvents, solvent ratios, and tertiary amine acceptors may be used successfully in this process. In some systems all of the bisphenol may not initially dissolve but will do so as the reaction proceeds and high molecular weight is attained.

Polymer Isolation. Polymers, isolated by a simple series of water or aqueous alcohol washes in a blender, followed by vacuum drying at 80° and storage at room temperature, frequently have been found to undergo a slow degradation in molecular weight over a period of several months or more. This degradation can be overcome or minimized in most cases by more elaborate isolation treatments, such as mild alkaline washes followed by washing to neutrality, dissolution in an organic solvent and reprecipitation, and use of monophenols as polymer end-capping agents.

Softening Temperatures. As indicated in table footnotes, the polymer softening temperatures were measured on dry powdered or granular polymer on a chrome-plated gradient temperature bar by the application of light sliding pressure. For amorphous or slightly crystalline polymers the softening range is very broad yet the initial point which is recorded here is usually readily determined within several degrees. Similar scales of values can be obtained by penetrometer tests on films and mechanically recorded elongations of films or fibers under light load. All of these measurements are very sensitive to polymer molecular weight, *i.e.*, exhibiting higher softening temperature ranges with increased molecular weight. For more exact studies it would be desirable to seek the maximum softening temperature of each composition by preparing samples of varying molecular weight. Molecular weight distribution should be considered as a possible factor as well.

Acknowledgment. Thanks are due to W. F. Dryden for excellent technical assistance and to C. E. Smullen for the preparation of fibers.

Polyquinoxalines Containing Flexibilizing Groups in the Chains

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ABSTRACT: Solution condensations of either 3,3′,4,4′-tetraaminodiphenyl sulfone or 3,3′4,4′-tetraaminobenzophenone in combination with various bisbenzils or glyoxals lead to high molecular weight polyquinoxalines. The effect of polymer structure on solubility, glass transition, and decomposition temperatures was investigated. Phenylated polyquinoxalines were readily soluble in chlorinated solvents while their structural nonphenylated analogs were insoluble. Polymer decomposition temperatures ranged between 430 and 520° depending upon structure. Polymer films cast from either chloroform or *m*-cresol solutions exhibited good toughness and flexibility.

The synthesis of polyquinoxalines[2-10] and polyphenylquinoxalines[11-14] has been reported by several investigators. Polyphenylquinoxalines exhibit superior solubility, and thermal and processing characteristics when compared to their nonphenylated analogs.[11,14,15] In addition to the beneficial effect derived from phenyl side group substitution, the introduction of the flexibilizing ether groups into the main polymer chain results in polyquinoxalines of improved melt flow characteristics.[16] On the other hand, the presence of ether groups results in a substantial lowering of the oxidative–thermal stability in these polymers.[15] In this investigation we examined some of these effects with polymers containing the chain flexibilizing sulfone and carbonyl groups.

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Experimental Section

Reactants. 3,3′,4,4′-Tetraaminodiphenyl Sulfone. To a stirred mixture of 300 ml of glacial acetic acid and 200 ml of acetic anhydride was slowly added 100 ml of 70% nitric acid. The mixture was frequently cooled during the addition of nitric acid to keep the temperature below 60°. The nitration mixture was cooled to 45° before 100 g of 4,4′-diacetamidodiphenyl sulfone was added in portions; the mixture was then stirred for 1 hr, and the resulting yellow precipitate was filtered, washed with acetic acid, and washed with ethanol. The crude product was then dissolved in 500 ml of hot dimethylacetamide and 1.5 l. of ethanol was added. Upon standing, 43.8 g (67%) of the product recrystallized as pale yellow needles, mp 145–148°.

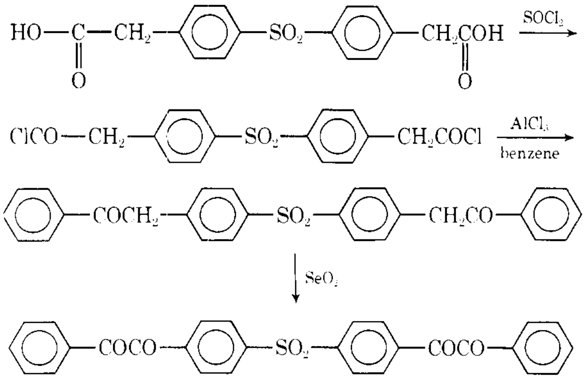
A mixture of 38.0 g of 3,3′-dinitro-4,4′-diacetamidodiphenyl sulfone, 150 ml of concentrated hydrochloric acid, and 250 ml of ethanol was refluxed for 2 hr. The mixture was then poured into 1 l. of water, and the precipitated solid was filtered and washed twice with water. The yield of the raw material, melting between 290 and 300°, was 29 g. Without further purification the product was used for the following reduction. A small amount recrystallized from water–ethanol (1 : 1) gave yellow crystals, mp 300–302°.

A mixture of 165 g (0.685 mol) of sodium sulfide nonahydrate dissolved in 250 ml of water and 23.0 g of 3,3′-dinitro-4,4′-diaminodiphenyl sulfone suspended in 250 ml of ethanol was refluxed for 1.5 hr. Upon cooling a pale orange solid precipitated which was filtered and washed several times with water. The product was recrystallized from 1 l. of water with 3 g of charcoal to give 12.5 g (66%) of white needles, mp 175–177°.[6] *Anal.* Calcd for $C_{12}H_{14}N_4O_2S$: C, 51.78; H, 5.07; N, 20.12. Found: C, 51.64; H, 4.88, N, 20.05.

3,3′,4,4′-Tetraaminobenzophenone was purchased commercially. Purification by recrystallization from a mixture of 9:1 water–pyridine gave polymer grade material (mp 218–218.5°).

4,4′-Sulfonyldibenzil was prepared as shown in Scheme I.

SCHEME I



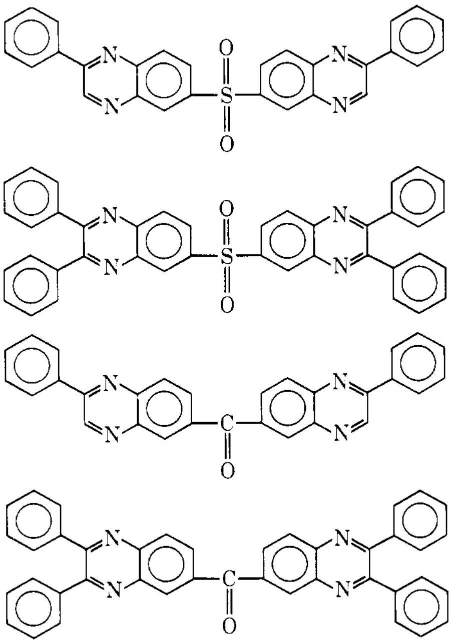
A mixture of 36.0 g (0.108 mol) of (4,4′-diphenyl sulfone)-diacetic acid, 32 g (0.270 mol) of thionyl chloride, and 180 ml of chloroform was refluxed for 6 hr. The solvent was evaporated under reduced pressure and the residual oil was poured into 500 ml of hexane giving 40.2 g of a tan solid, mp 105–108°.

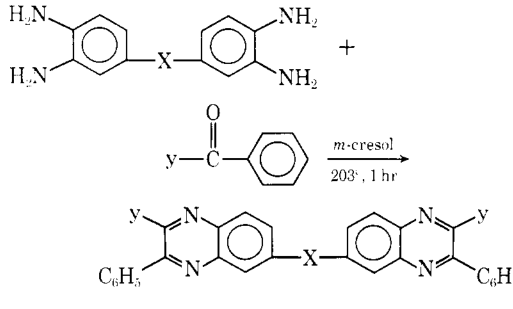
To a stirred mixture of 34.0 g (0.092 mol) of (4,4′-diphenyl sulfone)diacetic acid chloride in 150 ml of benzene was added in portions 40.0 g (0.30 mol) of aluminum chloride. The mixture was stirred for 6 hr at 45°. The flask content was cooled to room temperature and poured into a mixture of ice and hydrochloric acid, filtered, and washed with water. Recrystallization from glacial acidic acid gave 31.5 g (74%) of white product, mp 174–175°.

Sulfonylbis(*p*-desoxybenzoin), 22.7 g (0.050 mol), was added in portions to 12.2 g (0.110 mol) of selenium dioxide in 150 ml of glacial acetic acid. The flask content was refluxed for 6.5 hr and filtered hot. Upon cooling the filtrate, 18.0 g (76%) of white product crystallized, mp 164–166°. *Anal.* Calcd for $C_{28}H_{18}O_6S$: C, 69.70; H, 3.76; S, 6.64. Found: C, 69.94; H, 3.70; S, 6.88.

1,4-Bis(phenylglyoxalyl)benzene was prepared in 70% overall yield as described previously.[14] Recrystallization from acetic acid gave polymer grade material, mp 126–126.5° (lit.[17] mp 125–126°). 4,4′-Oxybisbenzil (mp 107°) was obtained according to a method reported by Ogliaruso.[18] 1,4-Diglyoxalylbenzene dihydrate (mp 143°) and 4,4′-diglyoxalyl diphenyl ether dihydrate (mp 122°) were prepared as described by Ruggli and Gassenmeier.[19]

Model Compounds. Four model compounds (III–VI) were prepared in nearly quantitative yields by solution condensations of the tetraamines with bisbenzil or phenylglyoxal as shown in eq 1





(1)

where X = SO_2 or CO and y = H or C_6H_5. The compounds were isolated by precipitation from methanol and were recrystallized from a mixture of 1:4 *m*-cresol–methanol. Model compounds I, II, VII, and VIII, prepared as previously

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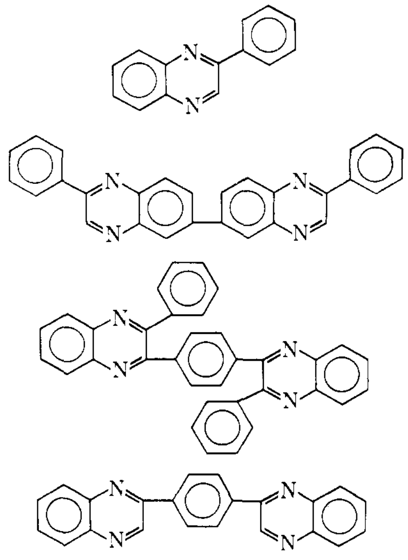


TABLE I

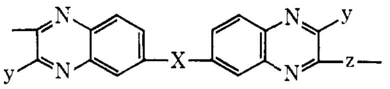
CHARACTERIZATION OF MODEL COMPOUNDS

Polymer no.	Mp, °C	Uv spectral data λ_{max}	 ϵ_{max}
I[a]		280	32,000
II[a]	314–315[b]	303	68,000
III	295–304[c]	295	40,330
IV	247–247.5	278	66,527
V	238–242	295	42,686
VI	232–232.5	285	79,740
VII	260–260.5	323	85,328
VIII	266–267[d]	292	28,214

[a] Values taken from ref 2a. [b] Lit.[2a] mp 314–315°. [c] Lit.[6] mp 274–275°. [d] Lit.[2a] mp 272–274°.

TABLE II

CHARACTERIZATION OF POLYMERS



Polymer no.	y	y	z	Calcd, % C	 H	 N	Found, % C	 H	 N	Inherent[a] viscosity	PDT[b]
I	SO_2	C_6H_5	*p*-Phenylene	74.48	3.68	10.22	74.76	3.54	10.10	1.68	490
II	SO_2	C_6H_5	*p,p'*-Diphenyl ether	74.98	3.78	8.75	74.89	3.78	8.67	1.47	490
III	SO_2	C_6H_5	*p,p'*-Diphenyl sulfone	69.75	3.51	8.13	69.78	3.60	7.98	0.76	490
IV	CO	C_6H_5	*p*-Phenylene	82.01	3.93	10.93	82.01	3.82	10.85	2.06	520
V	CO	C_6H_5	*p,p'*-Diphenyl ether	81.44	4.00	9.27	82.11	4.06	8.98	1.45	510
VI	CO	C_6H_5	*p,p'*-Diphenyl sulfone	75.44	3.71	8.58	75.43	3.63	8.41	1.03	510
VII	SO_2	H	*p*-Phenylene	66.65	3.05	14.13	66.62	3.04	13.98	0.73	450
VIII	SO_2	H	*p,p'*-Diphenyl ether	68.84	3.30	11.47	68.70	3.26	11.30	0.95	430
IX	CO	H	*p*-Phenylene	76.65	3.33	15.55	77.74	3.34	15.24	0.87	465
X	Co	H	*p,p'*-Diphenyl ether	76.98	3.57	12.38	76.62	3.69	11.57	0.55	440

[a] Determined in 98% sulfuric acid, 0.5% concentrated at 30°. [b] Determined by TGA at a heating rate of 5°/min under vacuum.

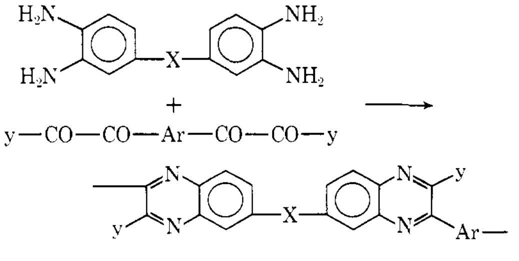
described,[2b,14] were also included in characterization studies (Table I).

Polymers. Polyphenylquinoxalines were prepared *via* solution condensation according to the following general procedure. A 100-ml three-necked, round-bottomed flask, fitted with stirrer, condenser, and gas inlet tube was charged with 0.01 mol of tetraamine and 50 ml of *m*-cresol. The flask was purged with nitrogen and 0.01 mol of the bisbenzil was added to the slurry at ambient temperature. A clear, viscous solution was obtained after addition was complete. The polymers were isolated as fibrous granular solids by precipitation from methanol and were then redissolved in either chloroform or *m*-cresol. Films were cast from these solutions by doctoring onto a glass plate and removing the solvent at 200° under reduced pressure.

Unsubstituted polyquinoxalines were prepared by a similar procedure. After addition of the bisglyoxal to a slurry of the tetraamine in *m*-cresol at ambient temperature a clear solution formed after 1 hr. Upon heating to 200° the polymers precipitated out and were isolated by quenching with methanol. The infrared spectra of the polymers at this stage of reaction showed the presence of glyoxal carbonyl bands at 1695 cm^{-1}, indicating incomplete reactions. Upon further heating the polymers at 300° for 2 hr in the solid state under a blanket of nitrogen the reaction was complete as indicated by the disappearance of this band. Characterization details are listed in Table II.

Results and Discussion

The formation of the polyquinoxalines is illustrated by the following general reaction



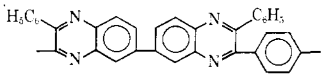
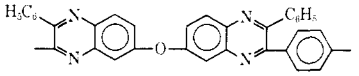
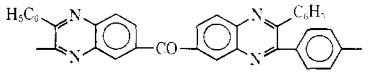
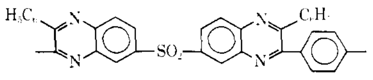
(2)

where X = CO, SO_2, y = H, C_6H_5, Ar = *p*-phenylene, 4,4'-diphenyl ether, 4,4'-diphenyl sulfone. The reaction of bisbenzils (y = C_6H_5) with either 3,3',4,4-tetraaminodiphenyl sulfone or 3,3',4,4'-tetraaminobenzophenone proceeded at room temperature to yield high molecular weight soluble final polyphenylquinoxalines. On the other hand, the reaction of bisglyoxals (y = H) with the tetraamines required more severe reaction conditions.

Apparently, due to the lower reactivity of the glyoxals, final unsubstituted polyquinoxalines could only be obtained after heating the precursors for 2 hr at 300° in the solid state. Characterization details are listed in Table II. The elemental composition, based on repeat unit structures, agreed well with the calculated values. Model compounds were further characterized by ultraviolet spectroscopy (Table I). Substituent effects in the pyrazine ring were investigated using the model compounds. Compounds IV and VI containing phenyl substituents in the 2 and 3 position of the pyrazine ring had λ_{max} values at 278 and 285 mμ while their monosubstituted analogs (compound III and V) showed λ_{max} values at 295 mμ. Apparently phenyl substitution produces an expected hypsochromic shift in these compounds. The ultraviolet spectra of model compounds II, III, and V were also examined for resonance interactions between the quinoxaline rings. A resonance effect is apparent in the spectrum of compound II containing the biphenyl linkage between the quinoxaline rings. A bathochromic shift of 23 mμ, relative to compound I, is indicative of a strong resonance interaction, which is confirmed by a twofold hyperchromic effect. The introduction of the sulfonyl or carbonyl group between the quinoxaline rings (III, V) produces a hypsochromic shift of 8 mμ with a corresponding decrease in band intensities. Apparently resonance interactions in the sulfone- and carbonyl-containing quinoxalines are somewhat less pronounced than in case of the biphenyl linkage.

Some polymer properties are listed in Table II. The inherent viscosities varied between 0.88 and 2.06 dl/g depending upon polymer structure. Owing to the greater reactivity of the bisbenzil monomers, higher viscosity values were obtained for the phenylated polymers (polymers I–VI). The effect of structure on polymer solubility was also investigated. All phenylated polymers could readily be dissolved in chloroform or tetrachloroethane in concentrations up to 20 wt % while their nonphenylated analogs were completely insoluble in these solvents. Nonphenylated polyquinoxalines containing diphenyl ether linkages could, however, be dissolved in phenol or *m*-cresol. Glass transition temperatures were obtained on thin films of polymers I and IV by means of dielectric loss measurements in an apparatus described previously.[20] The values obtained for these polymers were compared with polyquinoxalines described elsewhere[14] (Table III). The introduction of flexibilizing groups between the quinoxalines moieties produces a lowering in the T_g values. This lowering is most pronounced in case of the sulfonyl group.

TABLE III
EFFECT OF STRUCTURE ON T_g OF RELATED POLYPHENYLQUINOXALINES

	T_g, °C
	317
	298
	258
	212

The thermal stability of the polyquinoxalines was studied by thermogravimetric analysis. Polymer decomposition temperatures (PDT), defined as the temperature of onset of weight loss, varied from 430° for polymer III to 520° for polymer VI. The decomposition temperature of the phenylated polymers were distinctly higher than those of the unsubstituted polymers.

Acknowledgment. We wish to express our appreciation to P. M. Hergenrother for valuable technical discussions.

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