cm^{-1}, attributable to allene structure. This suggests a hydrogen transfer from one allylic group to the other in the termination in this polymerization, as proposed in the termination in the polymerization of cyclobutenes catalyzed with ruthenium(III) chloride.[2]

3 and **4** each converted butadiene to the polymer having similar microstructure and similar molecular weight to those obtained with the **1**–triphenylphosphine catalyst, respectively (see Table IV), while neither **3** nor **4** itself had a ruthenium–carbon bond. The facts stated above indicate that the propagation in the polymerization catalyzed by **3** or **4** proceeded through the almost same mechanism as that for the **1**–triphenylphosphine system. Accordingly, a ruthenium–carbon bond might be formed in the reaction of **3** or **4** with butadiene. This kind of the ruthenium–carbon bond formation may occur also in a reactivation process of the deactivated ruthenium species, which had presumably been produced in the termination reaction.

The tertiary phosphine, such as triphenylphosphine or tri-*n*-butylphosphine, was specific as the cocatalyst for **1** or **2** to polymerize butadiene, because triphenylarsine was never the effective cocatalyst in spite of the similarity of the structure between these two kinds of Lewis bases. Triaryl or trialkyl phosphite, alkyl phosphonotrithioite, or diaryl sulfide was also ineffective as the cocatalyst. In addition, triphenylarsine and triphenyl phosphite have a weaker σ-donating ability and a stronger π-accepting one than those of the tertiary phosphine, respectively.[25–27] These evidences indicate that the suitable degree of σ-donating ability and of π-accepting one, like those of tertiary phosphine, might be necessary for the activation of the π-allylic groups of **1** or **2** to polymerize butadiene.

Acknowledgment. The authors wish to acknowledge Mr. Akihiko Kuroiwa for his cooperation to the experiments by use of **2**, and thank Mr. Masakazu Fukuda for the infrared measurement of the polybutadienes.

(25) J. Chatt, S. Ahrland, and N. R. Davies, *Quart. Rev., Chem. Soc.*, **12**, 265 (1965).

(26) L. S. Meriwether and M. Fiene, *J. Amer. Chem. Soc.*, **81**, 4200 (1959).

(27) W. H. Horrocks, Jr., and R. C. Taylor, *Inorg. Chem.*, **2**, 723 (1963).

Polyquinoxalines Containing *p*-Phenylene Ether and *p*-Phenylene Moieties

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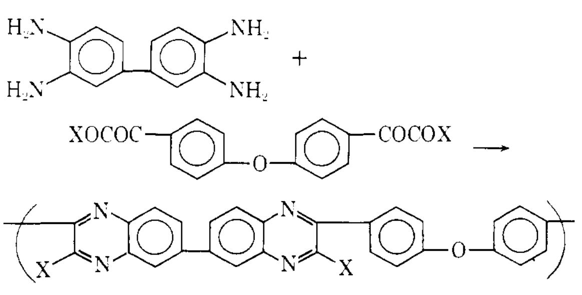
Received March 7, 1970

ABSTRACT: A series of quinoxaline polymers containing *p*-phenylene ether and *p*-phenylene moieties were prepared by polymerization of 3,3′-diaminobenzidine with various aromatic bisglyoxals in *m*-cresol. The glass transition temperature (T_g) of the polyquinoxalines varied from 133° for a polymer highest in *p*-phenylene ether content to 350° for a polymer containing rigid *p*-phenylene moieties. Ultraviolet and visible spectroscopic study showed the λ_{max} for the *p*-phenylene ether polymers to be about the same while pronounced bathochromic shifts in the λ_{max} were observed as the conjugated system was increased from *p*-phenylene to *p,p*′-biphenylene to *p,p*′-terphenylene in the *p*-phenylene polymers. Although thermal gravimetric analysis failed to show any distinct difference between the *p*-phenylene ether and the *p*-phenylene polymers, isothermal weight loss study at 400° in air showed that the *p*-phenylene polymers lost less weight after a given time than the *p*-phenylene ether polymers. Prior to polymer work, a series of quinoxaline model compounds was prepared to aid in polymer characterization.

Polyquinoxalines (PQ)[1–6] and polyphenylquinoxalines (PPQ)[7–9] have received considerable attention in recent years. These polymers are generally prepared by the reaction of an aromatic bis(*o*-diamine) such as 3,3′-diaminobenzidine with a bis(α-dicarbonyl) compound such as *p,p*′-oxybis(phenyleneglyoxal) or *p,p*′-oxydibenzil to yield a PQ or PPQ, respectively, as shown in eq 1.



X = H or C_6H_5 (1)

(1) G. P. de Gaudemaris and B. J. Sillion, *J. Polym. Sci., Part B*, **2**, 203 (1964).

(2) J. K. Stille and J. R. Williamson, *ibid., Part B*, **2**, 209 (1964); *Part A*, **2**, 3867 (1964).

(3) G. P. de Gaudemaris, B. J. Sillion, and J. P. Prévé, *Bull. Soc. Chim. Fr.*, 1793 (1964).

(4) P. M. Hergenrother, W. J. Wrasidlo, and H. H. Levine, "High Temperature Structural Adhesives," Final Summary Report, U. S. Navy Bureau of Naval Weapons Contract NOw 63-0420-c, San Diego, Calif., April 1964.

(5) J. K. Stille, J. R. Williamson, and F. E. Arnold, *J. Polym. Sci., Part A*, **3**, 1013 (1965).

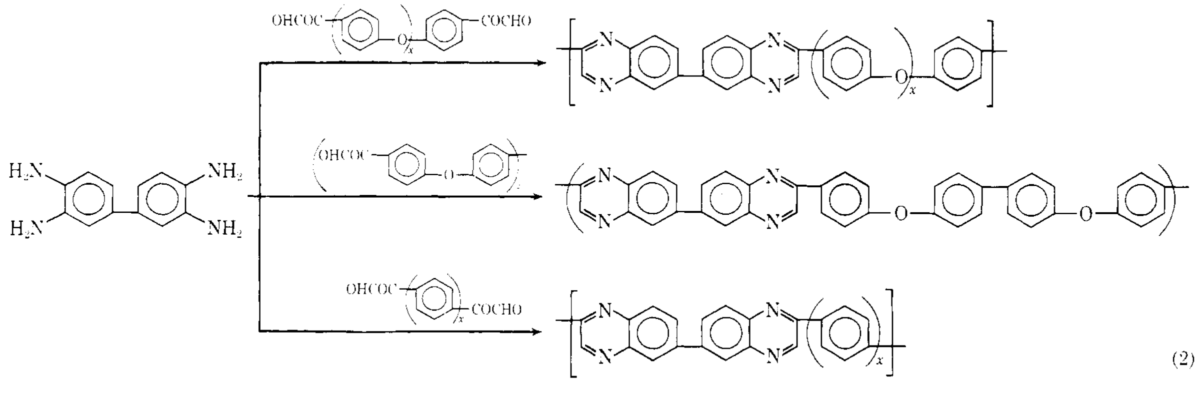
(6) J. K. Stille and F. E. Arnold, *ibid., Part A-1*, **4**, 551 (1966).

(7) P. M. Hergenrother and H. H. Levine, *ibid., Part A-1*, **5**, 1453 (1967).

(8) P. M. Hergenrother, *ibid., Part A-1*, **6**, 3170 (1968).

(9) W. Wrasidlo and J. M. Augl, *ibid., Part B*, **7**, 281 (1969); *ibid., Part A-1*, **7**, 3393 (1969); *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **10** (2), 1353 (1969).

Since the PQ have been shown to exhibit definite potential for use as high-temperature structural resins,[10] it was of interest to determine the extent to which the processability and certain physical properties such as the second-order transition temperature (T_g) of the PQ could be altered. Therefore, a series of PQ containing various amounts of *p*-phenylene ether and *p*-phenylene character were prepared as shown in eq 2.



(2)

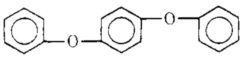
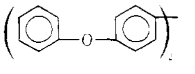
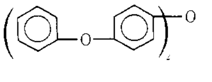
$x = 1, 2,$ and 3

Experimental Section

3,3′-Diaminobenzidine. This commercially available reactant was recrystallized from deoxygenated water under nitrogen to afford near-white crystals, mp 177–178 (lit.[11] mp 179–180°), after drying at 80° over phosphorus pentoxide, *in vacuo*.

Bis(*p*-phenoxyphenyl) Ether. The *p*-phenylene ether type of starting materials, *p,p*′-diphenoxybenzene, bis(*p*-phenoxyphenyl) ether, and *p,p*′-diphenoxybiphenyl shown in Table I, were prepared as indicated in the following representative procedure.

Table I
Phenylene Ether Reactants

Compd	Mp, °C	Lit. mp, °C	Recrystallization solvent
	69–71	74[a]	*n*-Hexane
	103–105	110[b]	Isopropyl alcohol
	147–149	151[c]	Benzene

[a] C. M. Suter and F. O. Green, *J. Amer. Chem. Soc.*, **59**, 2578 (1937). [b] J. Staudinger, *Makromol. Chem.*, **4**, 289 (1949). [c] H. Van Alphen, *Rec. Trav. Chim. Pays-Bas*, **50**, 415 (1931).

Potassium hydroxide (140 g, 2.5 mol) was added to phenol (330 g, 2.5 mol) at 150° and the temperature of the molten mixture was raised to 195° during 3 hr and maintained at 195° for 1 hr, allowing the water to distill off. The mixture was cooled to 135° and freshly precipitated copper (~10 g-atoms) and bis(*p*-bromophenyl) ether (328 g, 1 mol) were added. The dark red mixture was heated to 220° and stirred at 220° for 2 hr followed by pouring the partially cooled red mixture into dilute aqueous potassium hydroxide. After thorough washing with water, the crude tan solid (340 g, 96% crude yield) was recrystallized twice from isopropyl alcohol (3 l.) to provide bis(*p*-phenoxyphenyl) ether (200 g) as white crystalline flakes, mp 103–105°. The *p*-phenylene ether reactants are reported in Table I.

Bis[*p*-(*p*-acetylphenoxy)phenyl] Ether. The acetylation of the *p*-phenylene ether and *p*-phenylene compounds was performed according to the following typical procedure. A solution of bis(*p*-phenoxyphenyl) ether (95 g, 0.27 mol) and acetyl chloride (45 g, 0.58 mol) in methylene chloride (700 ml) was added during 2 hr to a slurry of anhydrous aluminum chloride (80 g, 0.60 mol) in methylene chloride (500 ml) at 0–5°. After complete addition, the dark brown mixture was stirred at ambient temperature for 18 hr followed by pouring onto ice and hydrochloric acid. The organic phase was separated and washed successively with water, aqueous sodium carbonate, and water. After drying over Drierite, the orange solution was partially concentrated followed by cooling to yield a near-white solid (80 g, 86% yield), mp 179–181°. Recrystallization from acetic acid (1 l.) afforded bis[*p*-(*p*′-acetylphenoxy)phenyl] ether (70 g), mp 180–181.5°. Characterization of the diacetyl compounds is given in Table II.

Bis[*p*-(*p*′-glyoxalylphenoxy)phenyl] Ether Dihydrate. The diacetyl compounds listed in Table II were oxidized to the corresponding bisglyoxal with selenium dioxide in acetic acid or dioxane and water as indicated in the following representative procedure.

A mixture of bis[*p*-(*p*′-acetylphenoxy)phenyl] ether (40 g, 0.09 mol) and selenium dioxide (22 g, 0.20 mol) in acetic acid (500 ml) was refluxed for 18 hr. The black reaction mixture was filtered hot and the filter cake washed twice with hot acetic acid (~250 ml). The combined acetic acid solution was cooled to yield a near-white solid (38 g, 84% yield), mp 151–155°. Recrystallization from a mixture of acetic acid and water (10:1) afforded bis[*p*-(*p*′-glyoxalylphenoxy)phenyl] ether dihydrate (31 g) as white plates, mp 154–156.5° dec. The bisglyoxals are listed in Table III.

Bis{*p*-[*p*′-(2-quinoxalinyl)phenoxy]phenyl} Ether (Model Compound III). All model compounds were prepared in the following manner. A mixture of *o*-phenylenediamine (2.16 g, 0.02 mol) and bis[*p*-(*p*′-glyoxalylphenoxy)phenyl] ether dihydrate (4.92 g, 0.01 mol) in *m*-cresol (25 ml) was heated to 200° during 2 hr and maintained at 200° for 1 hr under nitrogen. The clear yellow solution was cooled and diluted with methanol and water to precipitate an off-white solid (5.8 g, 95% yield), mp 186–190°. Recrystallization from benzene provided bis{*p*-[*p*′-(2-quinoxalinyl)phenoxy]phenyl} ether as an amorphous white solid, mp 190–191°. The model compounds are reported in Table IV.

Poly{2,2′-[*p,p*′-oxydi(*p*″-phenoxy)phenylene]-6,6′-di-

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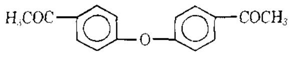
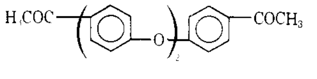
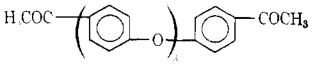
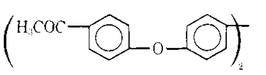
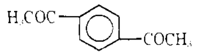
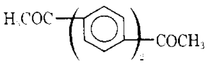
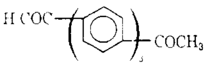
(10) P. M. Hergenrother and H. H. Levine, *J. Appl. Polym. Sci.*, **14**, 1037 (1970).

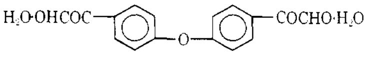
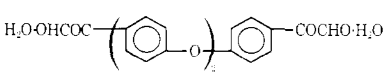
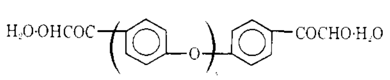
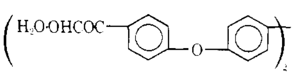
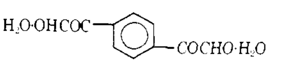
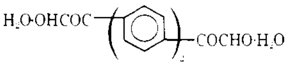
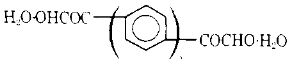
(11) H. Vogel and C. S. Marvel, *J. Polym. Sci.*, **50**, 511 (1961).

TABLE II
DIACETYL COMPOUNDS

Compd	Mp, °C	Lit. mp, °C	Formula	Calcd, %		Found, %	
				C	H	C	H
	100–101.5	100–101[a]	$C_{16}H_{14}O_3$				
	179–181	183.5[b]	$C_{22}H_{18}O_4$	76.28	5.23	76.17	5.16
	180–181.5	185[b]	$C_{28}H_{22}O_5$	76.69	5.05	76.62	5.20
	222–224	225[c]	$C_{28}H_{22}O_4$	79.63	5.21	79.47	5.36
	113–114	114[d]	$C_{10}H_{10}O_2$				
	189–190	190–191[e]	$C_{16}H_{14}O_2$				
	282–285	268–269[f]	$C_{22}H_{18}O_2$	84.05	5.77	83.98	5.84

[a] W. Dilthey, E. Bach, H. Grutering, and E. Hausdorfer, *J. Prakt. Chem.*, [2] **117,** 350 (1927). [b] R. G. Neville and R. W. Rosser, *Makromol. Chem.*, **123,** 19 (1969). [c] R. W. Rosser and R. G. Neville, *J. Appl. Polym. Sci.*, **13,** 215 (1969). [d] J. Ingle, *Ber.*, **27,** 2527 (1894). [e] C. V. Ferris and E. E. Turner, *J. Chem. Soc.*, **117,** 1147 (1920). [f] S. Patai, S. Schoenberg, and L. Rajbenbach, *Bull. Res. Council Israel*, **5A,** 257 (1956).

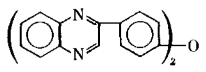
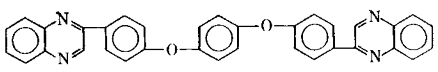
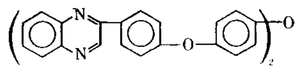
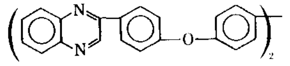
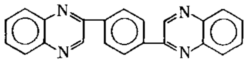
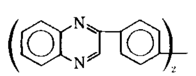
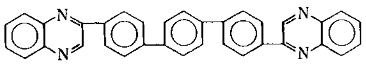
TABLE III
BISGLYOXAL MONOMERS

Compd	Mp, °C	Recrystallzn solvent	Formula	Calcd, %		Found, %	
				C	H	C	H
	141–143[a] dec	Dioxane + H_2O	$C_{16}H_{14}O_7$	60.38	4.43	60.27	4.39
	157–160 dec	Dioxane + H_2O	$C_{22}H_{18}O_8$	64.39	4.42	64.32	4.56
	154–156.5 dec	AcOH + H_2O	$C_{28}H_{22}O_9$	66.93	4.41	66.72	4.39
	178–180 dec	AcOH + H_2O	$C_{28}H_{22}O_8$	69.13	4.56	69.46	4.57
	162–164[b] dec	H_2O	$C_{10}H_{10}O_6$	53.10	4.46	53.29	4.35
	163–166 dec	AcOH + H_2O	$C_{16}H_{14}O_6$	63.57	4.67	63.42	4.72
	211–214 dec	AcOH + H_2O	$C_{22}H_{18}O_6$	69.84	4.80	69.63	4.86

[a] P. Ruggli and E. Gassenmeier [*Helv. Chim. Acta*, **22,** 496 (1939)] report mp 122°. [b] Lit. mp 110–111°; see footnote *a*.

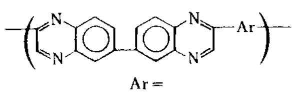
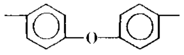
quinoxaline} (Polymer IIIP). The following procedure is representative for the synthesis of polyquinoxalines. Bis-[*p*-(*p*′-glyoxalylphenoxy)phenyl] ether dihydrate (5.025 g, 0.010 mol) was added to a slurry of 3,3′-diaminobenzidine (2.143 g, 0.010 mol) in *m*-cresol (30 ml) at ambient temperature under argon. Additional *m*-cresol (34.5 ml) was added to wash down the glyoxal and to adjust the concentration to 10% (solids content). The yellowish orange reaction mixture was stirred at ambient temperature for 1 hr followed by heating to 200° during 4 hr and stirring at 200° for 1 hr. The resulting viscous dark red solution was cooled and poured into methanol in a Waring Blendor to precipitate a fibrous yellow solid. After boiling in methanol followed by drying at 150°, *in vacuo*, for 4 hr, the resulting yellow intermediate polymer (6.0 g, 98.5% yield) exhibited an inherent viscosity (η_{inh}, 0.5% H_2SO_4 at 25°) of 0.62 (Table V). This polymer readily formed a solution in *m*-cresol (20% solid content) which was used to cast a transparent yellow film of

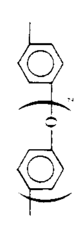
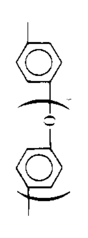
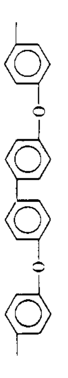
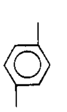
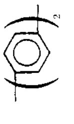
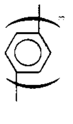
TABLE IV
QUINOXALINE MODEL COMPOUNDS

Model compound structure	Compd no.	Mp, °C	Color	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Uv spectrum[a] λ_{max}, mμ	Uv spectrum[a] $\epsilon \times 10^3$	Visible spectrum[a] λ_{max}, mμ	Visible spectrum[a] $\epsilon \times 10^3$
	I	171–173[b]	White	$C_{28}H_{18}N_4O$							221 263 315	35.0 22.0 38.0	524	36.7
	II	222–224	White	$C_{34}H_{22}N_4O_2$	78.75	4.28	10.80	79.02	4.37	10.71	221 263 315	43.0 27.5 46.9	522	37.9
	III	190–191	White	$C_{40}H_{26}N_4O_3$	78.67	4.30	9.17	78.55	4.20	9.11	218 262 315	49.0 28.5 56.8	523	43.4
	IV	229–231	Pale yellow	$C_{40}H_{26}N_4O_2$	80.79	4.41	9.42	80.60	4.58	9.16	263 310	32.5 50.5		
	V	266–267[c]	Yellow	$C_{22}H_{14}N_4$							276	39.0	437	39.8
	VI	261–262	Yellow	$C_{28}H_{18}N_4$	81.93	4.42	13.65	82.04	4.52	13.56	265 312	16.4 39.8	530	45.6
	VII	292–294	Yellow	$C_{34}H_{22}N_4$	83.93	4.56	11.51	84.47	4.86	11.16	230 265 350	30.2 24.5 45.2	615	39.4

[a] Obtained in sulfuric acid using a Cary Model 14 recording spectrophotometer. [b] Lit.[1] mp 172°. [c] Lit. mp 262°; see Table III, footnote *a*.

TABLE V
QUINOXALINE POLYMERS

 Ar =	Polymer no.	Intermediate polymer η_{inh},[a] dl/g	Intermediate polymer PST,[b] °C	Final polymer η_{inh},[a] dl/g	Final polymer T_g,[c] °C	Final polymer Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Ultraviolet spectrum[d] λ_{max}, mμ	Ultraviolet spectrum[d] $\epsilon \times 10^3$	Visible spectrum[d] λ_{max}, mμ	Visible spectrum[d] $\epsilon \times 10^3$
	IP	1.00	~315	1.62	280	$(C_{28}H_{16}N_4O)_n$	79.23	3.80	13.20	79.25	4.01	13.10	280 331	22.0 35.2	590	47.0

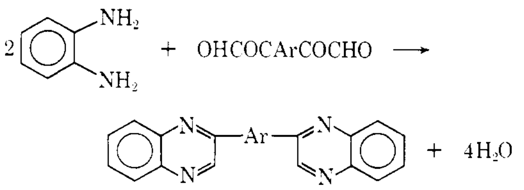
	IIP	0.58	~262	1.21	195	$(C_{34}H_{20}N_4O_2)_n$	79.06	3.90	10.85	78.98	3.88	10.84	283 333	29.9 42.3	584	47.5
	IIIP	0.62	~240	1.27	133	$(C_{40}H_{24}N_4O_3)_n$	78.93	3.97	9.20	77.89	3.95	8.99	284 333	30.0 46.0	585	48.0
	IVP	0.35	~253	0.82	213	$(C_{40}H_{24}N_4O_2)_n$	81.07	4.08	9.45	80.64	4.22	9.28	280 327	34.0 48.5		
	VP	0.61	>350	1.07	350	$(C_{22}H_{12}N_4)_n$	79.50	3.64	16.86	79.27	3.85	16.61	292	29.0	515	47.0
	VIP	0.73	~330	1.03	305	$(C_{28}H_{16}N_4)_n$	82.34	3.95	13.72	80.82	4.09	12.86	275 330	20.0 34.0	600	53.0
	VIIP	0.44	~340	0.91		$(C_{34}H_{20}N_4)_n$	84.28	4.16	11.56	82.20	4.22	10.48	284 365	24.0 36.0	675	37.5

[a] 0.5% solution in H_2SO_4 at 25°. [b] Polymer softening temperature, determined on Fisher-John melting point apparatus; PST taken as temperature when sample between cover slips becomes completely transparent upon applying slight pressure with a spatula. [c] Glass transition temperature, determined by dielectric loss measurements [W. Wrasidlo and J. M. Augl, *J. Polym. Sci., Part A-1*, **7**, 1589 (1969)]. [d] Obtained on sulfuric acid solutions using a Cary Model 14 recording spectrophotometer.

good flexibility and toughness. Further advancement of the polymer was effected by introducting a polymerization tube containing the yellow intermediate polymer under argon into an oil bath preheated to 350° and maintaining at 350° for 1 hr. During this heating phase, the polymer softened and foamed slightly. The η_{inh} of the final polymer (IIIP) was 1.27. Characterization of the polymers is given in Table V.

Results and Discussion

Model Compounds. A series of model compounds as shown in eq 3 and Table IV was prepared prior to polymer synthesis to aid in polymer characterization.



(3)

The model compounds were prepared in essentially quantitative yields by refluxing stoichiometric quantities of *o*-phenylenediamine and the bisglyoxal in *m*-cresol for 1 hr. The ultraviolet and visible spectral data for the model compounds are presented in Table IV. The wavelengths of maximum absorption ($\lambda_{\max}$) for the phenylene ether model compounds (I–IV) are essentially identical as would be expected since the length of the conjugated system is the same. Contrary to a recent report,[12] the ether oxygen atom does indeed disrupt the conjugated system. This is further shown in the ultraviolet and visible spectral data of the *p*-phenylene compounds (V–VII). As the length of the conjugation is extended, *e.g.*, from *p*-phenylene (V) to *p,p'*-biphenylene (VI) to *p,p'*-terphenylene (VII), a bathochromic shift of about 36–38 mμ in the $\lambda_{\max}$ in the ultraviolet region is observed. A more pronounced bathochromic shift is observed in the $\lambda_{\max}$ in the visible spectral region for the *p*-phenylene model compounds (V–VII). However, there is essentially no change in the $\lambda_{\max}$ in the visible spectral region for the *p*-phenylene ether model compounds (I–IV). It is interesting to note that the $\lambda_{\max}$ and molar extinction coefficient (ϵ) for compound I and VI are virtually the same. Apparently the major contribution of the excited state for compounds such as I arises from intramolecular charge-transfer transitions involving the ether oxygen atom which are stabilized in polar solvents (*e.g.*, sulfuric acid). Whereas, the major contribution to the excited state of compounds V–VII arises from resonance interaction.

Polymers

Quinoxaline polymers were prepared following a general method previously reported[7] by treating stoichiometric quantities of 3,3'-diaminobenzidine with the bisglyoxal in *m*-cresol. Relatively high molecular weight intermediate polymers were initially formed which were isolated by quenching in methanol, and further advanced by heating at 350° under argon. Characterization of the polymers is given in Table V. All the phenylene ether polymers (IP to IVP) and poly-

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(12) I. Schopov and N. Popov, *J. Polym. Sci., Part A-1*, **7**, 1803 (1969).

mer VIP formed dark red viscous solutions (10% solids content) in *m*-cresol from which transparent yellow films of good flexibility and toughness were cast. Polymer VP initially formed a dark red viscous solution which gelled. Polymer VIIP failed to form a complete solution in *m*-cresol even at 5% solids content.

The ultraviolet and visible spectral data (Table V) of the polymers agreed well with the trend displayed by the model compounds. The phenylene ether containing polymers (IP to IVP) exhibited essentially the same λ_{max} in both the ultraviolet and visible regions, again indicating that the conjugated system is disrupted by the ether oxygen atom. However, pronounced bathochromic shifts in the λ_{max} in both the ultraviolet and visible spectra are observed for the *p*-phenylene polymers (VP–VIIP). As the length of the resonance system increases in going from a *p*-phenylene (VP) to a *p,p'*-biphenylene (VIP) to a *p,p'*-terphenylene (VIIP) quinoxaline polymer, the λ_{max} increases from 292 to 330 to 365 mμ, respectively. This constitutes approximately the same magnitude of increase in the λ_{max} as observed for the corresponding model compounds (V–VII). Similar bathochromic shifts were also observed in the visible spectral region for polymers VP, VIP, and VIIP and as expected, the colors of the sulfuric acid polymers solutions were blue, yellow, and red, respectively.

The T_g's of the polymers as reported in Table VI were determined by dielectric loss measurements as recently reported[13] on films. As the amount of *p*-phenylene ether character of the polymer is increased in going from polymer IP to IIP to IIIP, the T_g of the polymer undergoes a pronounced decrease from 280 to 195 to 133°, respectively. Polymer IIIP exhibited a T_g of 133° which corresponds to the general temperature range where poly(*p*-phenylene oxide) shows similar transitions. A recent report[14] indicated that poly(*p*-phenylene oxide) exhibited a dispersion maximum at ~157° as determined by mechanical damping measurements.

Although the η_{inh} of the intermediate polymers varied (Table V) which indicates a difference in molecular weight, a trend in the polymer softening temperatures (PST) is evident. As the amount of phenylene ether character in the polymer increased (*e.g.*, polymer IIIP > IIP > IP), the PST decreased. In addition, polymer IVP with an η_{inh} of 0.35 exhibited at PST of ~253°, higher than that of polymer IIIP whose η_{inh} was 0.62.

Final polymers IIP, IIIP, and IVP exhibited behavior similar to that observed for thermoplastic materials. These polymers softened and became transparent under slight pressure at 300, 265, and 315°, respectively. Under pressure (<50 psi) at these temperatures, transparent flexible yellow films were formed.

The thermal and oxidative stability of the PQ were determined by thermogravimetric analysis (TGA) using a Du Pont 950 thermal gravimetric analyzer and isothermogravimetric analysis (ITGA). A representative TGA curve for polymer IP is shown in Figure 1 while the polymer decomposition temperatures (PDT) for the polymers are reported in Table VI. In general, the only trend observed by TGA was that the *p*-phenylene polymers (VP to VIIP) exhibit higher PDT in nitrogen than the *p*-phenylene ether polymers (IP–IVP). However, a definite trend was observed in the ITGA of the polymers at 400° in air (Figure 2). As found in

TABLE VI
POLYMER DECOMPOSITION TEMPERATURES OF POLYQUINOXALINES

Polymer	PDT, °C Air	PDT, °C Nitrogen	Residue at 1000° in nitrogen, %
IP	530	550	71.6
IIP	510	530	71.2
IIIP	510	520	61.4
IVP	535	560	74.0
VP	535	575	72.5
VIP	515	565	81.8
VIIP	525	600	80.8

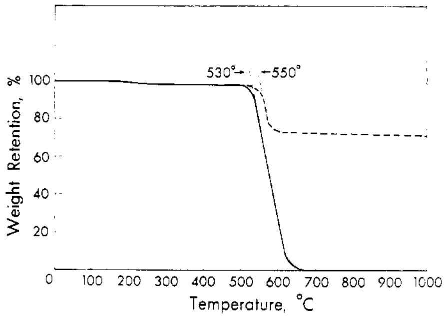

Figure 1. Thermogram of polyquinoxaline (polymer IP): ——, in air; ---, in nitrogen; ΔT = 7°/min; particle size <60 mesh.

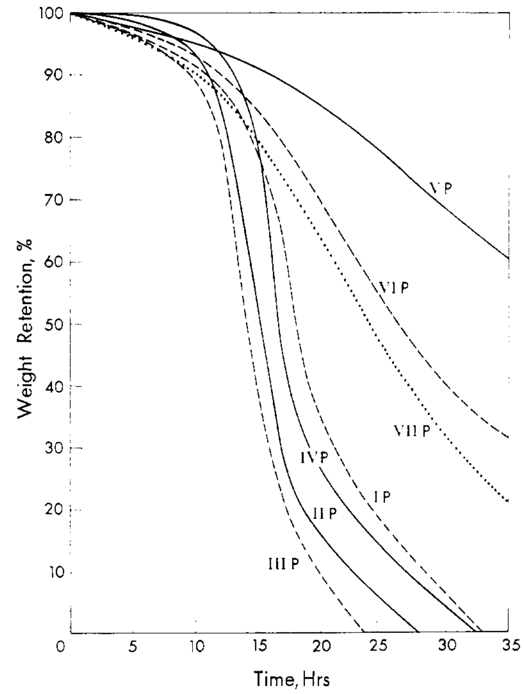

Figure 2. Isothermal weight loss curves of polyquinoxalines in air at 400°, particle size <60 mesh.

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(13) See Table V, footnote *c*.

(14) E. Butta, S. De Petris, and M. Pasquini, *J. Appl. Polym. Sci.*, **13**, 1073 (1969).

other polymer systems,[15] the *p*-phenylene polymers (VP to VIIP) exhibit somewhat better weight retention than the *p*-phenylene ether polymer (IP to IVP) after aging at 400° in air. This general trend is in agreement with recent reports[9,16] that the oxidative stability of polyquinoxalines containing diphenyl ether moieties is less than that of polyquinoxalines containing other moieties (*e.g.*, diphenyl sulfone, benzophenone, *p*-phenylene).

Acknowledgment. The authors would like to express their appreciation to Dr. J. M. Augl of Naval Ordnance Laboratory, Silver Spring, Md., for T_g determinations and to Mr. W. Wrasidlo for helpful discussions.

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(15) J. Preston, W. F. DeWinter, and W. B. Black, *J. Polym. Sci., Part A-1*, 7, 283 (1969).

(16) W. Wrasidlo, *ibid.*, in press.

Solid-State Polymerization of Hydrated Calcium Acrylate

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Received February 9, 1970

ABSTRACT: The dehydration of calcium acrylate dihydrate at 60° *in vacuo* involves a dihydrate → anhydrous transition with a significant loss of crystallinity. The ^{60}Co γ-ray initiated postirradition polymerization at 25 and 50° was strongly dependent on the degree of hydration. A marked inhibition of the postirradiation polymerization by oxygen was observed with maximum inhibition occurring at the hydrate composition for which maximum conversion was observed for polymerization *in vacuo*. The rate of polymerization is dependent on the short-range diffusion of monomer which, in turn, is dependent upon defects introduced during the dehydration process.

The solid-state polymerizations of various acrylate and methacrylate salts have been studied by Morawetz and coworkers.[1,2] These salts provided an excellent system for the study of solid-state postirradiation polymerization since their melting points are at much higher temperatures than that at which polymerization occurs, *i.e.*, premelting phenomena do not complicate the process. Postirradiation polymerizations were effected at 50 and at 101° with concurrent dehydration of the hydrated salts at the higher temperature. Markedly different yields were observed on postirradiation polymerization of different crystalline and amorphous modifications of calcium acrylate hydrate and anhydrate and of barium methacrylate hydrate and anhydrate. The polymerizations were, however, carried out in the presence of air and any possible effects of oxygen were ignored.

It seemed probable to us that a carefully controlled method of dehydration of the hydrated salts would permit a control of the extent of lattice defects and allow a study of the role of defects in the mechanism of postirradiation polymerization. Of the various factors which affect the kinetics and mechanisms of solid-state polymerization reactions, evidence is accumulating that such defects play a dominant role.[3-5] Indeed, Bamford and Eastmond state that, in general, polymerization will not occur in a perfect lattice.[6]

The present paper describes a study of the dehydration process in calcium acrylate dihydrate and the effect of intermediate degrees of hydration on the polymerization conversion *in vacuo* and in air.

Experimental Section

Monomer Preparation and Characterization. Calcium acrylate dihydrate was prepared by gradually adding a stoichiometric quantity of calcium hydroxide to a stirred, cooled aqueous solution (3 *N*) of freshly distilled acrylic acid, filtering, and allowing the filtrate to evaporate slowly. The monomer, obtained as long thin needles, was powdered in a mortar, sieved through a 40-mesh screen, and stored in a desiccator over a saturated solution of calcium chloride.

The work reported here was conducted on powdered material from several separately prepared batches, and the reproducibility of data between batches was excellent. The particle size distribution of the monomer powder was analyzed with Canadian standard sieves, 100 and 250 mesh. The distribution of particle sizes is shown as follows (the weight fraction is given in per cent): −40 + 100 mesh (149 μ), 20%; +250 mesh (63 μ), 20%; −250 mesh (<63 μ), 60%.

Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The results for the dihydrate were C, 33.04 ± 0.2; H, 4.62 ± 0.1 (calcd C, 33.02; H, 4.62). For the anhydrous material, C, 39.41; H, 3.62 (calcd C, 39.55; H, 3.32).

Dehydration experiments on the dihydrate were conducted by heating *in vacuo* at 60° using a Cahn electrobalance, Model RG. The extent of dehydration at any time could thus be controlled. The total weight loss was 16.5%, in excellent agreement with the theoretical value. These conditions of dehydration yield an amorphous product rather than the crystalline material derived from slow dehydration.[2]

The differential scanning calorimetry (dsc) studies were performed with a Perkin-Elmer dsc-1, using a 5°/min heating rate and a sample weight of 3–5 mg.

Infrared spectra in KBr pellets and as mulls in hexachloro-

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(1) (a) T. A. Fadner, I. D. Rubin, and H. Morawetz, *J. Polym. Sci.*, 37, 549 (1959); (b) H. Morawetz and I. D. Rubin, *ibid.*, 57, 669 (1962).

(2) J. B. Lando and H. Morawetz, *ibid., Part C*, 4, 789 (1964).

(3) V. A. Kargin, V. A. Kabanov, and G. P. Andrianova, *Polym. Sci. USSR*, 1, 106 (1960).

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(5) I. Kaetsu, N. Sagane, K. Hayashi, and S. Okamura, *J. Polym. Sci., Part A-1*, 4, 2241 (1966).

(6) C. H. Bamford and G. C. Eastmond, *Quart. Rev., Chem. Soc.*, 23, 271 (1969).