POLYBENZOXAZOLES, THEIR SYNTHESIS AND THERMAL DEGRADATION*†

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ONE way of creating heat-resistant polymers is to synthesize them with a rigid chain composed of aromatic and heterocyclic units.

A convenient method of producing such polymers is the two-stage synthesis in which the first stage produces a linear soluble polymer capable of intramolecular ring formation in the second stage. This is the method used to produce such highly heat-resistant polymers as polypyromellitimide [1], poly-1,3,4-oxadiazoles [2] and others.

The possibility of applying this method to the synthesis of polybenzoxazoles via a poly-*o*-oxyphenylamide stage has been demonstrated by several of us in [3], and independently by the Japanese authors of [4].

The present paper describes different polybenzoxazoles, some relationships connected with their formation and their behaviour on thermal degradation.

By low-temperature condensation of 3,3'-dioxybenzidine with acid dichlorides of dicarboxylic acids R (COCl)₂ in dimethylacetamide, we prepared polyoxamides (I, a–e) which, by thermal cyclodehydration were converted to the corresponding polybenzoxazoles (II, a–e):



where



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Polyoxamide (III) was also synthesized by the condensation of 4,4'-dioxy-3,3'-diaminodiphenylsulphone with isophthalylchloride, and polybenzoxazole (IV) produced from it. Table 1 shows η_{\log} of the synthesized I and also III, and the elementary analysis data. All the polyoxamides were prepared by polycondensation at approx. 0° and a total concentration of approx. 1 mole/l. for the initial components. The yields were approximately quantitative.



Fig. 1. Variation in η_{\log} of polyoxamide Ia in the process of polycondensation.

TABLE 1. POLYOXAMIDES

Polyox- amide	$\eta^*_{ m log}$	Found, %			Formula	Theoretical, %			
		C	н	N		C	н	N	
Ia	0.87 69.10 4.50 7.64		$C_{20}H_{14}N_2O_4$	69.36	4 ·05	8.08			
\mathbf{Ib}	1.07	68.36	4.44	7.79	$C_{20}H_{14}N_2O_4$	69.36	4.05	8.08	
\mathbf{Ic}	0.69	62.09	3.88		$C_{18}H_{12}N_2O_5$	64·3 0	3.57	8.33	
Id	0.72	64.58	4 ·01	11.30	$C_{19}H_{13}N_3O_4$	65.75	3.75	12.10	
Ie†	0.87	64.43	4 ·18	8.27	$C_{16}H_{12}N_2O_4$	$64 \cdot 86$	4.06	9.46	
III	0.50	57.56	4 ·0 4	6.30	$\mathbf{C_{20}H_{14}N_2O_6S}$	58.53	3.49	6.83	

* The logarithmic viscosity No. of polymer solutions in concentrated H₂SO₄ (0.5 g/100 ml solution, 25°).

† Synthesis carried out in 2.5% solution of LiCl in dimethylacetamide.

On the example of polyoxamide Ia it was established that η_{\log} rises rapidly during the first hour of the polycondensation reaction, and then remains practically unchanged (Fig. 1). Polyoxamide Ia forms strong transparent flexible films and is capable of fibre formation.

The solubility of the different polyoxamides is given in Table 2.

The structure of the polyoxamides is confirmed by the elementary analysis data, and also by comparing their IR spectra with those of specially synthesized model compounds.*

Solvent	Polyoxamide							
	Ia	Ib	Ic	Id	Ie	III		
96% H ₂ SO ₄	++-	+++	++	++	++	+++		
Dimethylformamide + 5% LiCl	++	-+- +-	++	++	++	++		
N-methylpyrrolidone	++	+	-+-	++		++		
Dimethylsulphoxide	++	+	+	++		++		
Dimethylacetamide	+		_	++	í	++		
Dimethylformamide	_	—	—	++		+++		

TABLE 2. Solubility of polyoxamides at approx. 20° *

* ++ Soluble; + partially soluble or swells; - insoluble.

Except for III, all the polyoxamides are coloured materials; in some cases the colouring is quite intense. For instance, polyoxamide Ib is bright yellow and Ie red. The colouring of the polyoxamides may be connected with conjugation in the macromolecule chain, which might occur via the tautomeric isoamide form with formation of a π -conjugated system:



The ring formation of polyoxamides also seems to take place via the isoamide form.

Table 3 sets out the conditions of ring formation, η_{\log} and the elementary analysis data.

Polybenzoxazoles IIa and IIb are soluble in concentrated H_2SO_4 and insoluble in amide solvents, even with the addition of LiCl. Polybenzoxazoles IIc-e are insoluble in concentrated H_2SO_4 , which seems to point to crosslinking in the process of ring formation.

* IR spectra were recorded and discussed by V.P. Bazov.

Polybenzoxazole	Cyclization conditions*		Weight loss on cycliza-	nț	Found, %			Formula	Theo	oretical, %	
	temper- ature, °C	time, hr	tion, % of theoret- ical	108	С	н	N		С	н	N
IIa IIb IIc IId IIe IV	350 360 360 350 350 280	$ \begin{array}{r} 1 \cdot 0 \\ 4 \cdot 0 \\ 4 \cdot 0 \\ 3 \cdot 0 \\ 2 \cdot 0 \\ 2 \cdot 5 \end{array} $	100 98 92 98 97 93	0.99 1.55 - - - 0.51	76·30 75·25 70·36 71·82 69·78 62·51	3.11 3.34 3.07 3.24 3.81 3.04	8·50 - 12·70 9·02 -	$\begin{array}{c} C_{20}H_{10}N_2O_2\\ C_{20}H_{10}N_2O_2\\ C_{18}H_8N_2O_3\\ C_{19}H_9N_3O_2\\ C_{16}H_8N_2O_2\\ C_{20}H_{10}N_2O_4S\ddagger \end{array}$	77.40 77.40 72.00 73.30 73.80 64.16	3·24 3·24 2·67 2·89 3·07 2·71	9.03 9.03 9.33 13.50 10.77 7.49

TABLE 3. POLYBENZOXAZOLES

* Cyclization at approx. 10⁻⁸ mm.

† η_{\log} of initial polyoxamide indicated in Table 1.

[‡] Found, %: S 8.00. Calculated, %: S 8.56.

The structure of the polybenzoxazoles prepared is confirmed by the elementary analysis data and the IR spectra. Comparison of the spectra of the polybenzoxazoles and the corresponding polyoxamides shows that the absorption bands in the 3400–3100 cm⁻¹ range have disappeared (valency vibrations of bound OH- and NH-groups) and also the 1660 cm⁻¹ band (amide I) after heat treatment of the polyoxamides, and also shows the appearance of absorption bands typical of the benzoxazoles ring [5], at 1630, 1555 and 935 cm⁻¹. Similar changes in the IR spectra are found on converting model oxyamides to model benzoxazoles.

The polybenzoxazoles synthesized have brilliant luminescence. For poly-2,2'-(*m*-phenylene)-6,6'-dibenzoxazole (IIa) the absorption band lies in the range $410-580 \text{ m}\mu$.*

Although in some cases the weight loss on the cyclization of polyoxamides under the conditions indicated in Table 3 is the same as the theoretical, amide units may nevertheless be partially retained in the polymer. For instance, after heating up to 350°, where the weight loss of polyoxamide Ia is practically the same as for total cyclization, there still remains a weak absorption band around 1660 cm⁻¹ (amide I) (Fig. 2 spectrum 1) in the IR spectrum of polymer IIa. This band does not disappear completely until the polymer is heated at 420–430° (Fig. 2, spectrum 2), and it is accompanied by the slight liberation of volatile products consisting of water vapour and CO_2 . After such treatment IIa even becomes partially soluble in concentrated H_2SO_4 .

The thermal degradation of the polybenzoxazoles was studied at a residual pressure of 10^{-3} mm on a heat balance with a response of 0.5 mg.

Polybenzoxazoles IIa-d were stable on vacuum heating to $520-530^{\circ}$; above this temperature there was marked liberation of volatile products. But even after heating at 480° an absorption band around 1690 cm^{-1} appeared in the IR

* According to R. N. Nurmukhametov.

spectrum of the polymer (Fig. 2, spectrum 3), and appears to be associated with a partial change in the benzoxazole structure. Apart from this, no other changes in the spectrum were found.

The initial rate of polybenzoxazole degradation at 600° is as follows (%/min): IIa 0.46, IIb 0.34, IIc 2.5, IIe (at 546°) 3.0.



FIG. 2. IR spectra of polybenzoxazole IIa film (spectra recorded on UR-10 spectrophotometer): 1-1 hr at 350°, 2-1 hr at 420-430°; 3-2 hr at 480°.

FIG. 3. Degradation kinetics of polybenzoxazole IIa: $1-571^{\circ}$, $2-599^{\circ}$, $3-610^{\circ}$.

The kinetics of thermal degradation at different temperatures were studied on the example of polybenzoxazole IIa. The results are shown in Fig. 3. The rate of degradation shows an appreciable reduction after a loss of 15-20% in weight; after a loss of about 25% the degradation almost ceases.

Calculated from the initial rates, the apparent activation energy of degradation is approx. 70 kcal/mole, i.e. commensurate with the binding energy.

The main volatile products of the thermal degradation of polybenzoxazole IIa were identified from the IR and mass spectra, and found to be CO, CO_2 , H_2 , HCN, C_6H_6 and CH_4 . The formation of methane in the process of thermal degradation seems to be due to dimethylacetamide residues in the polymer, which were formed at the polycondensation stage by reaction of the end acid chloride groups of the polyoxamide with the solvents [6].

After degradation (degradation temperature 615° , weight loss 24.4%) the residue is a black powder (found, %: C 82.52; H 3.34; N 6.56). The IR spectrum has none of the absorption bands characteristic of the benzoxazole ring, but there are intense bands at 1690 and 1620–1610 cm⁻¹.

G. I. BRAZ et al.

EXPERIMENTAL

Model compounds. N,N'-di-(o-oxyphenyl)-2,5-furandicarboxamide. A solution of 1.92 g (0.176 mole) o-aminophenol in 7 ml dimethylacetamide was put into a 3-necked flask with an agitator and thermometer, and at approx. 20° a solution of 1.7 g (0.088 mole) 2,5-furandicarboxyldichloride [7] in absolute benzene added dropwise. The reaction mass was stirred for another 5 hr, treated with water and the residue washed with a certain amount of alcohol. The yield was 80%, m.p. 261–262° (from alcohol; the sealed capillary tube was lowered at 200°).

Found, %: C 64·18; H 4·12. $C_{18}H_{14}N_2O_5$. Calculated, %: C 64·00; H 4·15.

The following oxamides were synthesized in the same way. N,N'-di-(o-oxyphenyl)isophthalamide, yield 70%, m.p. 230° (from aqueous alcohol).

> Found, %: C 69.00; H 4.85; N 8.58. C₂₀H₁₆N₂O₄. Calculated, %: C 69.00; H 4.60; N 8.10.

N,N'-di-(o-oxyphenyl)terephthalamide, yield 89%, m.p. 294–295° (from pyridine; sealed capillary tube lowered into apparatus at 250°*).

Found, %: C 68.99; H 4.71. $C_{20}H_{16}N_2O_4$. Calculated, %: C 69.00; H 4.60.

N,N'-di-(o-oxyphenyl)fumaramide, yield 95%, m.p. 251-252° (from alcohol; capillary lowered at 220°).

Found, %: C 64.62; H 4.78. C₁₆H₁₄N₂O₄. Calculated, %: C 64.42; H 4.73.

N,N'-dibenzoyl-3,3'-dioxybenzidine, yield 76%, m.p. 308-309° (from pyridine; capillary lowered at 300°*).

Found, %: C 73.52; H 4.83; N 6.02. C $_{26}H_{20}N_2O_4$. Calculated, %: C 73.56; H 4.71; N 6.63.

N,N'-di-(furoyl-2)-3,3'-dioxybenzidine, yield 86%, m.p. $319-320^{\circ}$ (from *m*-cresol; capillary lowered at 298° *).

Found, %: C 65.72; H 4.19; N 6.84. C₂₂H₁₆N₂O₆. Calculated, %: C 65.40; H 3.96; N 6.94.

N,N'-dinicotinoyl-3,3'-dioxybenzidine, yield 86%, m.p. $292-294^{\circ}$ (from pyridine; capillary lowered at 275° *).

Found, %: C 67.69; H 4.51. C₂₄H₁₈N₄O₄. Calculated, %: C 67.70; H 4.22.

Cyclization of N,N'-di-(o-oxyphenyl)-2,5-furandicarboxamide. 0.22 g oxamide was heated for 4 hr in an ampoule at 300°. Yield of unpurified 2,5-di-(benzoxazolyl-2)furan 72%, m.p. 240–242° (from dioxane).

Found, %: C 71.49; H 3.46. $C_{18}H_{10}N_2O_3$. Calculated, %: C 71.50; H 3.32.

Synthesized in the same way: 1,3-di-(benzoxazolyl-2)benzene, yield 89%, m.p. 233-234° (from dioxane), from published data m.p. 229-230° [8]; 2,2'-diphenyl-6,6'-dibenzoxazole, yield of unrefined material 78%, m.p. 248-249° (from benzene); published data on m.p. 249-250° [9].

* Rate of temperature rise 4-5°/min.

Polybenzoxazole synthesis

Polyoxamides. Poly-3,3'-di-oxydiphenylisophthalamide (Ia). To a solution of 0.500 g (0.00232 mole) 3,3'-dioxybenzidine [10] in 5 ml dimethylacetamide at 0° agitated in an argon atmosphere, 0.470 g (0.00232 mole) isophthalylchloride was poured in all at once. Stirring was continued at the same temperature for 2 hr. To separate the polymer, the reaction mixture was heated until a transparent viscous liquid was formed and a thin layer was deposited on glass plates which were then immersed in water. The polymer separated as thin transparent films which were washed in water until free from Cl^- ions, then washed in methanol and vacuum dried at 100° to a constant weight.

Polyoxamides Ib-d and III were synthesized in the same way (Table 1).

Polybenzoxazoles. Poly-2,2'(*m*-phenylene)-6,6'-dibenzoxazole (IIa). 0.1006 g polyoxamide Ia was heated for 1 hr at $120^{\circ}/10^{-3}$ mm; 0.0045 g sorbed moisture was removed as a result. Then the specimen was kept for 1 hr at $350^{\circ}/10^{-3}$ mm; weight loss 0.010 g.

Polybenzoxazoles IIb-e and IV (Table 3) were prepared in the same way.

CONCLUSIONS

(1) Polyoxamides have been prepared by the low-temperature polycondensation of 3,3'-dioxybenzidine and 4,4'-dioxy-3,3'-diaminodiphenylsulphone with acid dichlorides of dicarboxylic acids in dimethylacetamide, and then converted to the corresponding polybenzoxazoles by thermal cyclodehydration.

(2) The polybenzoxazoles prepared are stable when vacuum heated to $52\,0{-}530^\circ$.

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