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POLYKETOAMINES AS A NEW TYPE OF HETEROCHAIN POLYMER*

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(*Received* 9 *January* 1969)

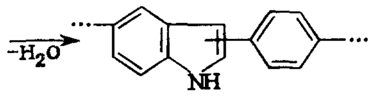
A LARGE number of heat-resistant polymers with heterocycles in the main chain has now been synthesized, but those having heterocycles condensed with a benzene ring are of the greatest current interest to investigators [1, 2].

Our aim in this investigation was to study polymers with indole rings in the chain.

To synthesize these polymers we used Bishler's reaction referred to in reference [3]. Starting with di-α-helogenomethylketones and aromatic diamines we obtained polyketoamines which may then be converted by dehydrocyclization into polymers with indole rings in the chain:

$$n\mathrm{NH_2—Ar—NH_2}+n\mathrm{BrCH_2CO—Ar'—COCH_2Br}\rightarrow$$

$$\rightarrow (2n—1)\ \mathrm{HBr}+\mathrm{H—[—NH—Ar—NHCH_2CO—Ar'—COCH_2—]}_n\mathrm{—Br}$$



This paper gives the results of a study of the first stage in this reaction leading to the formation of linear polyketoamines. Polyketoamines were synthesized by us from 4,4'-bis(bromoacetyl)benzene and 4,4'-bis-(bromoacetyl)diphenyloxide and 4,4'-diaminodiphenyl (benzidine), 4,4'-diaminodiphenyloxide, 4,4'-diaminodiphenylmethane, 4,4'-bis-(methylamino)diphenylmethane and 3,3-bis-(4-aminophenyl)phthalide (anilinephthalein).

Before proceeding to synthesize the linear polyketoamines we prepared and studied a number of model compounds (Table 1). In particular we prepared

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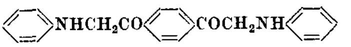
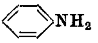
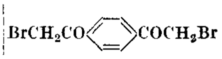
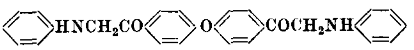
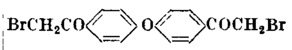
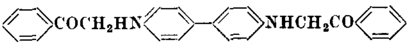
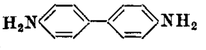
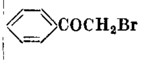
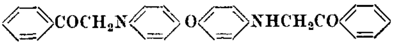
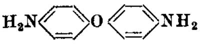
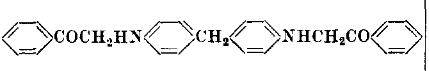
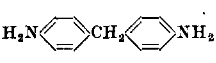
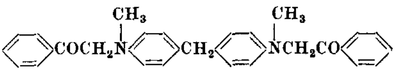
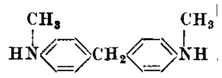
TABLE 1. SYNTHESIS AND

Polymer No.	Formula of compounds	Starting materials	
		aromatic amine	α-halogenomethylketone
1			
2		Ditto	
3			
4			Ditto
5			» »
6			» »

* *Notation*: DMFA—dimethylformamide; DMAA—dimethylacetamide; HMPA—hexamethylphosphamide; TCE—tetrachloroethane; s—soluble; i—insoluble

and characterized 4,4′-bis-(phenylamino)-N,N′-diacetyldiphenoxide (Table 1, No. 2) from aniline and 4,4’-bis-(bromoacetyl)diphenyloxide and 4,4′-bis-(phenylamino)-N,N′-diacetylbenzene (Table 1, No. 1) from aniline and 4,4′-bis-(bromoacetyl)benzene following the procedure described in reference [4] for phenylamino-N-acetylbenzene.

The structure of the resulting compounds was confirmed by elemental analysis and IR spectroscopy. The IR spectrum has a band in the region of 1690 cm^{-1} characteristic of the carbonyl group, and in the region of 3400 cm^{-1} there is the band of N–H valency vibrations.

In addition we prepared model compounds that have not been described in the literature: these are based on α-halogenomethylketones and aromatic diamines. Bromoacetophenone was used as the α-halogenomethylketone, and all the aromatic diamines listed above were used as second initial compcnents.

A 70 to 90% yield of compounds (see Table 1, Nos. 3–6) was obtained by carrying out the reaction in aprotonic dipolar solvents such as dimethylacetamide (DMAA) and hexamethylphosphamide (HMPA) with heating up to 100° for several hours.

The polyketoamines were synthesized in HMPA because the resulting polymer is hardly soluble in DMAA (several minutes after the start of the reaction the polymer separates out in this solvent). Besides this HMPA has more basic properties than DMAA, and is a better acceptor of the hydrogen bromide liberated in the reaction [5]. The structure of the polymers is confirmed by their IR spectra which are identical to those of the model compounds. The properties of the product polymers and the conditions under which they were synthesized are given in Table 2.

PROPERTIES OF MODEL COMPOUNDS

Reaction conditions		Yield, %	Properties of model compounds					
solvent	temp. and time		m.p. (in capillary), °C	solubility			found, %	calc., %
				DMFA DMAA HMPA	TCE	dioxane		
Aniline	20°–1 hour	75	193–195	s	s	s	C 77·34 H 6·16 N 7·32	C 76·72 H 5·85 N 8·13
Ditto	Ditto	66	186–188	s	s	s	C 76·71 H 5·59 N 6·36	C 77·04 H 5·54 N 6·41
DMAA	20°–2 hours 100°–10 hours	83	In preheated unit 225–230	s	i	i	C 80·16 H 5·36 N 6·07	C 79·98 H 5·80 N 6·42
Ditto	Ditto	85	In preheated unit 232–235	s	i	i	C 77·53 H 5·16 N 5·87	C 77·04 H 5·54 N 6·41
HMPA	20°–4 hours 50°–7 hours 80°–3 hours	88	In preheated unit 150–155	s	s	s	C 79·01 H 5·93 N 7·05	C 80·16 H 6·03 N 6·44
Ditto	Ditto	93	118–120	s	s	s	C 80·39 H 7·05 N 5·97	C 80·50 H 6·53 N 6·05

All the polyketoamines except the polymer based on 4,4′-bis-methylamino)-diphenylmethane are infusible, and barely soluble in organic solvents. Figures 1 and 2 show the thermomechanical and thermogravimetric curves of the polymer based on benzidine and 4,4′-bis-(bromoacetyl)diphenyloxide.

The solubility of the polyketoamines based on the same di-α-halogenomethylketone (4,4′-bis-(bromoacetyl)diphenyloxide) and different aromatic diamines such as benzidine, diaminodiphenyloxide and anilinephthalein rises slightly on changing from the benzidine polymers to anilinephthalein polymers (Table 2, Nos. 2–4); the improvement in solubility was admittedly considerably less than expected on introducing the diphenyloxide group, and particularly the side phthalide group, into the polymer chain: for example a side phthalide group introduced into polyamides, polyimides and polyarylates improves their solubility considerably [9–6].

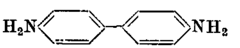
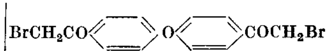
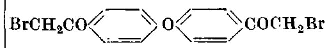
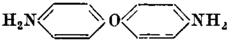
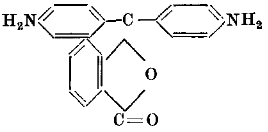
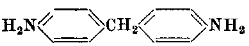
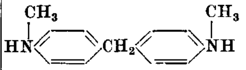
Soluble and fusible polymers were prepared from secondary aromatic diamines (e.g. 4,4′-bis-(methylamino)diphenylmethane), and also on separating from the reaction medium polymers based on primary diamines, such as 4,4′-diaminodiphenylmethane, using dilute hydrochloric acid (~ 10%) (see Table 2, Nos. 6, 7).

EXPERIMENTAL

The DMAA and HMPA used in the experiments were dried over phosphorus pentoxide and vacuum-distilled. Their constants agreed with published information.

Bromoacetophenone, 4,4′-bis-(bromoacetyl)benzene and 4,4′-bis-(bromoacetyl)diphenyl oxide were synthesized by the methods described in references [10–14], and had melting points well in accordance with published data.

TABLE 2. SYNTHESIS AND PROPERTIES OF POLYKETOAMINES $-[-RN-Ar-NR-CH_2-CO-Ar'-CO-CH_2-]_n-$ PREPARED BY POLYCONDENSATION IN HMPA, AT 20°, IN AN INERT ATMOSPHERE

Polymer No.	Starting material		Yield, %	Properties of polymers					
	aromatic diamine	di-α-halogenomethylketone		m.p. (in capillary), °C	solubility*				reduced viscosity at 25° for 0·5% solution in TCE/P, dl/g
					H_2SO_4	DMFA DMAA HMPA	TCE/P	N-methylpyrrolidone	
1			76	> 400	s	i	i	i	—
2	Ditto		70	Ditto	s	i	i	i	—
3		Ditto	76	„ „	s	i	p.s.	i	0·14(0·43% solution)
4		„ „	90	„ „	s	i	p.s.	s	0·20(0·40% solution)
5		„ „	90	„ „	s	i	i	i	—
6†	Ditto	„ „	75	In preheated unit 250–260	s	s	s	s	0·15
7‡		„ „	95	145–155	s	s	s	s	0·35

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* *Notations*· TCE/P—mixture of tetrachloroethane and phenol (3 : 1 by weight); p.s.—partially soluble; other notations as in Table 1.

† Polymer was separated as its hydrochloride.

‡ Polycondensation carried out under the following temperature conditions: 20°—1hr, 50–60°—5hr, 70–80°—5hr. 90–100°—3hr.

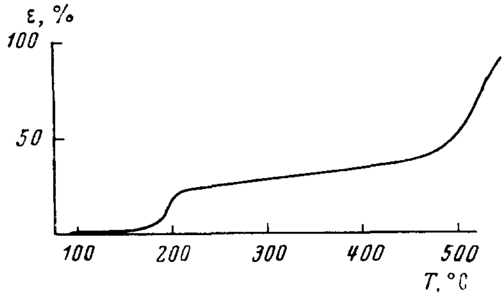

FIG. 1

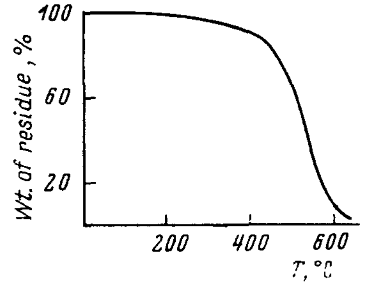

FIG. 2

FIG. 1. Thermomechanical curve of polyketoamine based on benzidine and 4,4′-bis-(bromoacetyl)diphenyloxide, recorded in air with 100 g loaded on a punch 4 mm in diameter.

FIG. 2. Dynamic thermogravimetric analysis of polyketoamine based on benzidine and 4,4′-bis-(bromoacetyl)diphenyloxide, obtained with an MOM (Hungarian) derivatograph under dynamic conditions, rate of temperature rise 4·5 deg/min, in air.

Aniline and benzidine were vacuum-distilled. Their constants corresponded to the published data.

The other diamines used in the experiments were synthesized by the methods described in [15–18], and had melting points well in accordance with the published data.

4,4′-bis-(phenylamino)-N,N′-diacetyldiphenyloxide. 0·5 g of 4,4′-bis-(bromoacetyl)-diphenyloxide was dissolved in 9 ml of aniline at room temperature, while stirring in a current of inert gas. 5 min after the dissolution of 4,4′-bis-(bromoacetyl)diphenyloxide a pale yellow precipitate separated out from the reaction mixture. Stirring was continued for one hour longer, then the reaction mixture was decanted into ethanol. The precipitate was filtered, washed with ethanol, and with a 2% aqueous solution of hydrochloric acid also with water, and with ethanol, and was then recrystallized from a benzene–ethanol mixture (1 : 1 by weight). The yield was 70% of theory; m.p. 186–188°.

Found, %: C 76·71; H 5·59; N 6·36. $C_{28}H_{24}O_3N_2$. Calculated, %: C 77·04; H 5·54; N 6·41.

N,N′-Diphenacylbenzidine. 0·80 g of bromoacetophenone was added to a solution of 0·37 g of benzidine in 5 ml of DMAA at room temperature. The reaction mixture was stirred at room temperature for 3 hr in a current of inert gas, and then at 100° for ~10 hr, before being decanted into a mixture of water and ethanol. The resulting precipitate was filtered, washed with an acetic acid solution in water (1 : 30 by weight), then with water, and also with ethanol and ether. The yield was 70% of theory; m.p. 228–230° (in a preheated unit).

Found, %: C 80·16; H 5·36; N 6·07. $C_{28}H_{24}O_2N_2$. Calculated, %: C 79·78; H 5·80; N 6·42.

Synthesis of polyketoamine based on benzidine and 4,4′-bis-(bromoacetyl)diphenyloxide. 0·60 g of benzidine was added to a solution of 1·34 g of 4,4′-bis-(bromoacetyl)diphenyloxide in 14·5 ml of HMPA, and the reaction mixture was stirred in a current of inert gas at room temperature for ~6 hr, The reaction mixture was decanted into methanol and the polymer which separated out was filtered, washed with an acetic acid solution in water (1 : 30 by weight), as well as with water and ethanol, before being vacuum-dried at 30–40°. Yield of polyketoamine—76% of theory; the polymer does not melt below 400° (above 400° it decomposes).

Found, %: N 6·17. ($C_{28}H_{22}O_3N_2$). Calculated, %: N 6·45.

Synthesis of polyketoamine based on 4,4′-bis-(methylamino)diphenylmethane and 4,4′-bis (bromoacetyl)diphenyloxide. 0·30 g of 4,4′-bis-(methylamino)diphenylmethane was added to a solution of 0·55 g of 4,4′-bis-(bromoacetyl)diphenyloxide in 7·5 ml of HMPA, and the mixture was stirred in a current of inert gas at room temperature for 1 hr, then at 50–60° for 6 hr, at 70–80° for 6 hr, and at 100° for 3 hr. The reaction mixture was decanted into methanol and the polymer that separated out was filtered, washed with methanol as well as with water and ethanol, and then vacuum-dried at 30–40°. Yield of polyketoamine—95% of theory; the polymer melts in a capillary at 145–155°; reduced viscosity of a 0·5% solution of the polymer in a mixture of tetrachloroethane and phenol (3 : 1 by weight) 0·35 dl/g. The polymer is readily soluble in amide solvents and in a mixture of phenol and tetrachloroethane.

Found, %: N 6·19. $C_{31}H_{28}O_3N_2$. Calculated, %: N 5·88.

CONCLUSIONS

Heterochain polymers of a new type, namely polyketoamines, have been obtained by reacting 4,4′-bis-(bromoacetyl)diphenyloxide and 4,4′-bis-(bromoacetyl)benzene with different aromatic diamines. The properties of the obtained polymers have been investigated.

Translated by R. J. A. HENDRY

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