(3) The element composition and molecular weight of the polydioxyarylenephosphonitrilates obtained have been determined, and their infrared spectra taken.

Translated by G. Modlen

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PREPARATION OF REGULAR POLYSUCCINAMIDES*

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In recent years, much attention has been given to work on the synthesis of high molecular weight compounds having fibre-forming properties. Thus two basic problems are being solved: (1) the establishment of the connection between the structure of the initial monomers, their tendency to form high molecular compounds and the properties of the polymers obtained; (2) the creation of macromolecules with alternate rigid and elastic links.

The present investigation was initiated with the aim of developing a method of obtaining regular polysuccinamides.

It is known that succinic acid has not been used for the preparation of polyamides because of its tendency to form 5-membered rings [1–3], as a result of which, during the condensation of succinic acid with diamides at 160–200°C, succinimide rings are formed at the ends of the growing polyamide chain, and these lead to rapid termination of the growing chain and consequently to the formation of low molecular weight products. Thus, during the condensation of succinic acid with hexamethylenediamine, and oligomer was obtained with 4–8 units and a molecular weight of 1500–3000 [4].

We have previously shown [5], that succinimide rings easily open up in the cold and at room temperature under the action of aqueous solutions of amines with the formation of the corresponding diamides.

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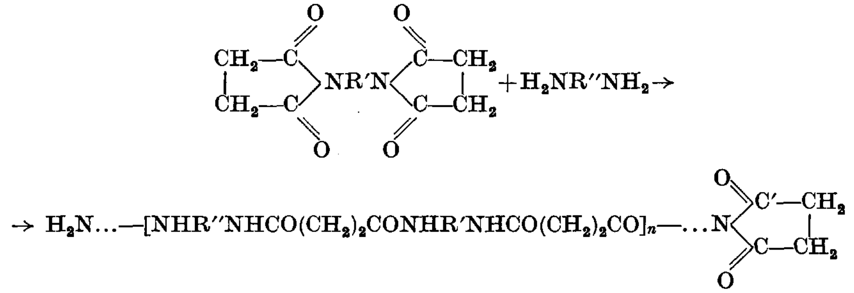
On this basis, succinic acid was not selected as the initial product for the preparation of polyamides, but rather its cyclic bifunctional derivatives, namely, disuccinimides, and their reaction with various diamides was studied.

It has been shown that at 0–20°C the reaction of disuccinimides with diamines involves the opening up of the rings according to the equation:



where $R' = (CH_2)_6$; $CH_2C_6H_4CH_2$; $R'' = (CH_2)_2$; $(CH_2)_4$; $(CH_2)_6$; $CH_2C_6H_4CH_2$.

In this way, migration copolymerization takes places with the migration of hydrogen from the amine to the imide nitrogen with the formation of linear polyamides of regular structure (with an aminogroup and an imide ring as end groups), in which R' and R'' alternate in a fixed sequence and may be selected.

With the process of polyamide formation managed in this way, halting of chain growth can take place either because of hydrolysis with the formation of an end carboxyl group, or because diffusion is made more difficult through an increased viscosity in the reaction medium.

To suppress hydrolysis, the reaction was carried out in a water-alcohol medium. The 1770 cm^{-1} frequency, coresponding to the carboxyl group, was completely absent from the infrared spectra of all the synthesized polyamides. This is confirmation of the fact that no hydrolysis took place.

The optimum conditions for carrying out the migration copolymerization are at a temperature of 0–20°C (although in certain cases opening up of the succinimide rings also takes place at 10°C), in a water-alcohol medium, pH=9–9·5. In a neutral medium (in dry dioxan and dimethyl formamide) the reaction does not take place even at 150°C. In these experiments, the initial diimide was evolved.

A number of homogenous and mixed polyamides of regular structure, not previously described with molecular weights up to 15,000–20,000 and melting points of 260–300°C, was obtained. Experimental results are presented in Tables 1 and 2.

X-ray structure analysis showed that all the polyamides synthesized are crystalline. The structure was demonstrated by the element analysis and infrared spectroscopy. The following characteristic bands are present in all the spectra: 1690–1780 cm^{-1} belonging to the 5-membered imide ring; 3500–3300 cm^{-1} corresponding to the aminogroup; and the 1550 cm^{-1} frequency, typical of the amide group.

TABLE 1. POLYAMIDES FROM HEXAMETHYLENEDISUCCINIMIDE AND HEXAMETHYLENEDIAMINE

Reaction temper-ature, °C	Medium	pH	Polyamide (fraction, insoluble in alcohol)									Polyamide (fraction, soluble in alcohol)		
			m.p., °C	yield, %	mol. wt.	found, %			calculated, %			m.p., °C	yield, %	mol. wt.
						C	H	N	C	H	N			
20	Dioxan	9–9·5	260–270	60	8700	60·29	9·34	13·95	60·6	9·14	14·1	250	10	
5	Water	9·0	300	15·1	11,200	60·15	9·06	14·33	60·6	9·14	14·1	270	50	6000
0	Aqueous alcohol	9·5	260–270	70	7200	—	—	—	—	—	—	—	—	
20	Ditto	9·5	260–280	70	16,000	60·27	9·39	14·03	60·6	9·14	14·1	160–180	7	4500
20	”	9–9·5	255–265	91	20,000	—	—	—	—	—	—	—		
78	96% alcohol	8·5–9	255–265	55	8500	—	—	—	—	—	—	240–250	8	—
20	Dry dioxan	7·0	Initial diimide evolved											
101	Ditto	7·0	Ditto											
154	Dry dimethylformamide		”											

TABLE 2. POLYAMIDES FROM HEXAMETHYLENEDISUCCINIMIDE AND VARIOUS DIAMINES

Initial products		Reaction temperature, °C	Medium	pH	Polyamide (fraction, insoluble in alcohol)									Polyamide (fraction, soluble in alcohol)		
								found, %			calculated, %					
diimide	diamine				m. p., °C	yield, %	mol. wt.	C	H	N	C	H	N	m. p., °C	yield, %	mol. wt.
Hexamethylenedisuccinimide	Tetramethylenediamine	−10	Aqueous alcohol	9–9·5	~300	17·5	11,700	58·83	9·0	15·11	58·6	8·69	15·21	200–215	30	4600
Ditto	Ditto	20	Ditto	9–9·5	255–260	26	13,300	58·78	8·55	15·07	58·6	8·69	15·21	180–190	47·6	4100
”	”	20	”	9–9·5	240–260	20	15,100	—	—	—	58·6	8·69	15·21	190–200	58·6	—
”	Ethylenediamine	20	Aqueous alcohol	9–9·5	250–265	13·0	10,000	56·3	8·14	16·07	56·47	8·23	16·47	200–220	24	2000
”	*para*-Xylylenediamine	−10	Ditto	9–9·5	262–282	27·0	7000	63·59	7·71	13·35	63·4	7·68	13·46	180–200	30	2070
”	Ditto	20	”	9–9·5	250–260	28·0	11,000	62·91	7·67	13·11	63·4	7·68	13·46	180–200	44·5	—
para-Xylylenedisuccinimide	”	20	Aqueous dioxan	9–9·5	280–290	42·3	6000	67·22	5·54	11·66	67·03	5·58	11·73	210–220	18·0	—

EXPERIMENTAL

Hexamethylene and tetramethylenedisuccinimide were obtained following the method described in [4], by heating succinic acid with the diamines for 2 hours at 180–200°C. After recrystallization from aqueous alcohol, hexamethylenedisuccinimide with a melting point of 116–117°C and tetramethylenedisuccinimide with a melting point of 160°C were obtained.

para-Xylylenedisuccinimide was obtained by first heating succinic anhydride with *para*-xylylenediamine for 3 hours at 160–180°C. The yield of the diimide amounted to 40% of the theoretical, melting point 242–243°C (from alcohol).

Found, %: C 64·25; H 5·44; N 9·39,

$C_{16}H_{16}O_4N_2$. Calculated, %: C 64·0; H 5·33; N 9·33.

Migration copolymerization was carried out by mixing equimolecular quantities of the disuccinimides with the diamines: (a) in boiling solvents (dry dioxan, dry dimethyl formamide, 96% alcohol); (b) in water and in aqueous alcohol at -10–$+20$°C.

Elimination of the initial diamide from the polyamides was carried out by extraction of the alcohol in a Soxhlet apparatus. By boiling in alcohol, a fraction was evolved, soluble in ethanol. The molecular weight for all the products was determined by viscosimetry in *meta*-cresol. The maximum molecular weight amounts to 16,000, melting point 260–300°C. For the fractions soluble in ethanol, the molecular weight did not exceed 6000 and the melting point 200–240°C. The experimental results are collected in Table 1 and 2.

As may be seen from Table 1, the reaction does not proceed in dry dioxan and dimethyl formamide at the boiling point. In boiling 96% alcohol the reaction does proceed but a product is obtained with a fairly small yield and with a lower molecular weight than in the cold. When the reaction is carried out in a water-alcohol medium at 0 and 20°C (Tables 1 and 2) from 30–90% of homogeneous and mixed polyamides are formed.

The authors wish to express their thanks to Ye. I. Pokrovskii for taking the infrared spectra and also to the analytical laboratory of the Institute for High Molecular Compounds, for carrying out the analyses.

CONCLUSIONS

(1) It has been shown that polysuccinimides with molecular weights of up to 20,000 may be obtained by the migration copolymerization of disuccinimides with diamines.

(2) The migration copolymerization reaction takes place at low temperatures of from -10 up to 78°C in a water-alcohol medium at pH=9–9·5.

(3) *para*-Xylylenedisuccinimide, not described previously, has been obtained and characterized.

(4) The following compounds have been obtained and characterized: polyhexamethyleneethylenesuccinamide, polyhexamethylenetetramethylenesuccinamide, polyhexamethylenesuccinamide, polyhexamethylene-*paru*-xylylenesuccinamide, poly-*para*-xylylenesuccinamide.

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POLYMERIZATION AND COPOLYMERIZATION OF TETRACYANOETHYLENE CATALYSED BY PARAMAGNETIC POLYMERS*†

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IN previous works [1–11] contributions bave already been made about the activation of the reaction capacity of compounds with a conjugated system by means of paramagnetic polymers (the "local activation" effect). The presence in such polymers of fractions of macromolecules with distributed electrons, the macromolecules being bound in strong π-complexes with the diamagnetic polymerhomologues, determines the observed ESR (Electron Spin Resonance) paramagnetism of the compounds with a developed conjugated system [13]. The experimentally established fact that anthracene and a number of other polynuclear aromatic compounds transform upon heating in the presence of PMP (paramagnetic particles) into polymer substances [5] as well as data about the transformation of polyconjugated compounds containing PMP into even higher polymer products, indicates that in these cases a formely unknown type of polymerization reaction is taking place, which one of us has conditionally termed "quasiradical polymerization" [1, 2].

The polymerization reaction under consideration is evidently connected with the formation of donor–acceptor complexes both in the stage of the creation of an active centre, as well as in the stages of chain growth and termination. In connection with this, it was of interest in the present work to clarify the possibility

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