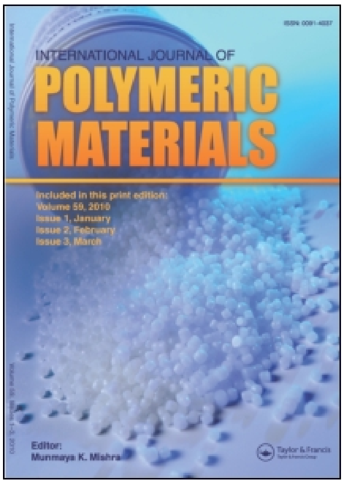

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Heterofunctional Condensation of 4,6-bis(*n*-aminophenyl)pyrimidine with α,ω)-bis(diethylamino- and α,ω-bis(β-carboxylethyl)diorganosiloxanes

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Heterofunctional Condensation of 4,6-bis(*n*-aminophenyl)pyrimidine with α,ω-bis(diethylamino- and α,ω-bis(β-carboxylethyl)diorganosiloxanes

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Copolymers containing siloxane fragments and aromatic heterocycles in their main chains of macromolecules have been synthesized. Heterofunctional condensation of 4,6-bis(*n*-aminophenyl)pyrimidine with α,ω-(diethylamine)- and α,ω-bis(β-carboxylethyl)diorganosiloxanes was conducted at 1:1 molar ratio of initial components at 150–180°C. Thermogravimetric characteristics of the synthesized thermally stable copolymers have been investigated.

KEY WORDS Heterofunctional condensation, copolymers, thermogravimetry, siloxanes.

INTRODUCTION

Development of many areas in modern science and technology requires the development of polymer materials possessing specific characteristics. The solution of this problem is closely linked to the conception of new types of polymers and the methods for their synthesis. The opportunities for functional modification of characteristics of polymers have led us to explore the synthesis of polymers with organoinorganic molecular chains. Because of their potential use, the polyorganosiloxanes and polyamides occupy a very significant place among high molecular compounds. The representatives of these groups of polymers meet the requirements of modern applications.

Considering the valuable characteristics of polyamides and polyorganosiloxanes, synthesis of hybrid polymers containing siloxane fragments and aromatic heterocycles in the main chains of macromolecules appeared most interesting.

EXPERIMENTAL

IR spectra were recorded on Spectrometer UR-20. Films of 0.01 mm thickness and tablets of KR_2 were used as samples.

Initial α,ω-bis(diethylamino)dimethylsiloxanes were obtained by aminolysis of α,ω-dichlorodimethylsiloxanes by the use of diethylamine according to the known methods,[1] α,ω-bis(β-carboxyethyl)diorganosiloxanes were obtained via hydrosililation of acrilic acid by α,ω-dihydrodiorganosiloxanes in presence of a catalyst of Spyer.[2]

1. Interaction of 4,6-bis(*n*-aminophenyl)pyrimidine with bis(diethylamino)dimethylsiloxane

3 g of 4,6-bis(*n*-aminophenyl)pyrimidine and 2.22 g of bis(diethylamine)dimethylsiloxane) were placed in a two-neck flask supplied with a thermometer, a tube for nitrogen flushing, a direct condenser and a receiver supplied with calcium chloride tube. The mixture was heated to 150–180°C for 2 hr, and diethylamide isolated during the reaction was distilled. Reaction was stopped after sublimation of 0.73 g diethylamine. Reaction mixture was dissolved in dimethyl formamide and reprecipitated by hexane. 3.18 g of Copolymer I (90.5% of theoret.) was obtained.

Copolymers II–VI were obtained similarly to Copolymer I.

2. Interaction of 4,6-bis(*n*-aminophenyl)pyrimidine with α,ω-bis(β-carboxyethyl)dimethylsiloxane ($n = 4$)

2.6 g of 4,6-bis(*n*-aminophenyl)pyrimidine, 4.26 g of α,ω-bis(carboxyethyl)-dimethylsiloxane ($n = 4$) and 10 ml of dioxane were placed in three-neck flask. The reaction mixture was heated to 150–180°C for 3 hr under vacuum. Copolymer obtained in this way was isolated by filtration, dissolved in dimethylformamide and reprecipitated by hexane. Copolymer was dried in vacuum dryer for 5 hr at 70°C. 6.02 g (93% of theoret.) of a copolymer (VII) was yielded.

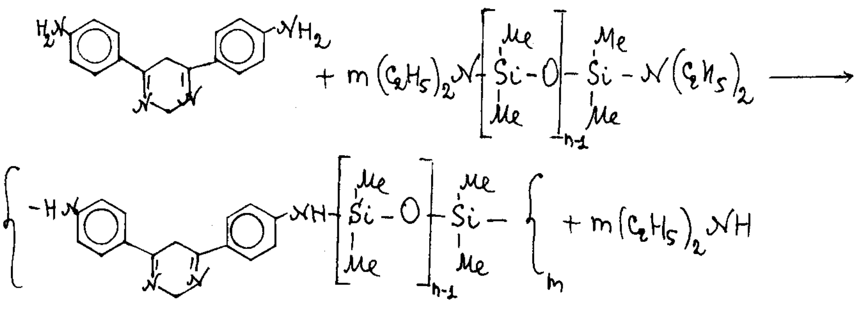
Copolymers VIII–XIV were obtained similarly to Copolymer VII.

RESULTS AND DISCUSSION

According to the reference 3, amino- or alkyl amino groups at the silicon atoms may participate in condensation reaction with different organic amines with the release of ammonia or amine.

In the present study high-temperature heterofunctional condensation (HFC) reaction of 4,6-bis(*n*-aminophenyl)pyrimidine with α,ω-bis(diethylamine)dimethylsiloxanes has been considered. The proposed method is rather simple, but copolymers obtained are characterized by relatively low molecular masses.

In order to accomplish synthesis of linear copolymers with ordered interchange of heterocyclic siloxane rings in a polymer chain, reaction of interaction of 4,6-bis(*n*-aminophenyl)pyrimidine with α,ω-bis(diethylamino)dimethylsiloxanes was carried out, which proceeded by the following scheme:



where n = 1 (I); 6 (II); 12 (III); 25 (IV); 50 (V); 100 (VI).

High-temperature HFC was conducted at 1:1 molar ratio of initial components, in a current of dry nitrogen both in a block and in solution. In block conditions, reaction mass was heated to 180°C till homogeneous mixture was obtained, then reaction was continued in vacuum at P = 3–5 mm of mercury column in the temperature interval of 150–180°C up to achieving constant viscosity. For complete isolation of diethylamine evolving in the process of reaction, the mixture was scavenged by dry inert gas. Polymers obtained as a result of the described method did not need any extra purification, because, diethylamine isolated as a secondary reaction product is characterized by low boiling point and under conditions of synthesis is completely removed from the reaction mixture. The process of reaction was controlled according to the release of diethylamine (Figure 1).

All the synthesized copolymers are highly flexible stable products of brown

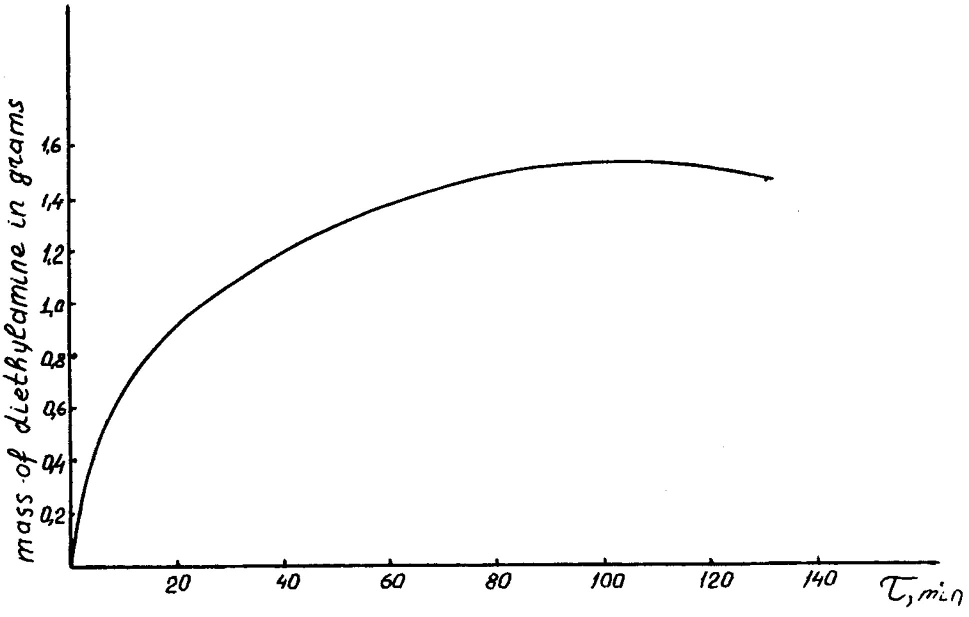


FIGURE 1 Rate of diethylamine isolation during condensation reaction of 4,6-bis(n-aminophenyl)pyrimidine with α,ω-bis(diethylamino)dimethylsiloxane (n = 6).

TABLE I

Some physico-chemical characteristics and elementary analysis data of copolymers on the base of 4,6-bis(*n*-aminophenyl)-pyrimidine and α,ω-bis(diethylamino)dimethylsiloxanes

No	(SiO)n	Yield %	intr. of 1% sol. in DMFA at 20°C	FOUND, %				FORMULA	CALCULATED, %			
				C	H	N	Si					
1	2	3	4	5	6	7	8	9	10	11	12	13
I	1	90,5	0.25	67,70	6,00	8,07	9,30	$C_{18}H_{18}N_4Si$	67,92	5,66	17,61	8,81
II	6	89,5	0,31	48,62	6,70	8,20	25,00	$C_{28}H_{48}N_4Si_6O_5$	48,84	6,98	8,14	24,42
III	12	88,0	0,37	42,81	7,03	5,25	29,26	$C_{40}H_{84}N_4Si_{12}O_{11}$	42,40	7,42	4,95	29,68
III^1	12	13	0,34	40,50	7,0	5,15	28,80	$C_{40}H_{84}N_4Si_{12}O_{11}$	42,40	7,42	4,95	29,68
III^2	12	18	0,39	41,70	6,98	5,10	29,0	$C_{40}H_{84}N_4Si_{12}O_{11}$	42,40	7,42	4,95	29,68
III^3	12	32	0,38	42,50	7,10	5,30	29,80	$C_{40}H_{84}N_4Si_{12}O_{11}$	42,40	7,42	4,95	29,68
IV	25	87,0	0,42	37,91	7,35	2,23	33,14	$C_{66}H_{162}N_4Si_{25}O_{24}$	37,82	7,74	2,67	33,42
V	51	87,5	0,49	35,75	7,84	1,60	35,10	$C_{10}H_{318}N_4Si_{55}O_{54}$	35,24	7,91	1,39	35,54
VI	101	88,0	0,56	33,50	7,35	0,25	36,98	$C_{218}H_{606}N_4Si_{101}O_{100}$	33,95	7,86	0,73	36,70

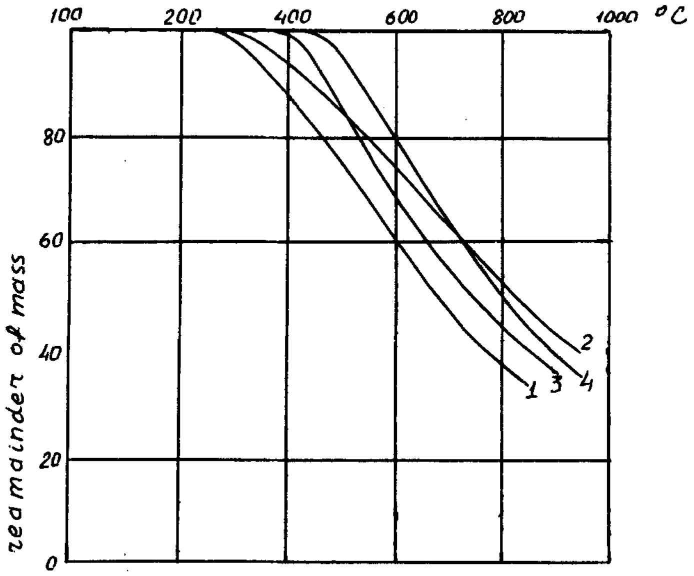


FIGURE 2 Thermogravimetric curves of copolymers with dimethyllisoxane fragments in chain: 1—I ($n = 1$); 2—II ($n = 6$); 3—IV ($n = 25$); 4—VI ($n = 100$); (at V = 5° per min, in air).

colour, soluble in organic solvents. But at long-term standing they lose their ability to dissolve.

Some of the physical and chemical characteristics and the data of elementary analysis of the synthesized copolymers are presented in Table I.

Thorough analysis of the fraction mixture of the reaction products has shown that reaction may proceed in two directions: intermolecularly with the formation of copolymers, and via intramolecular cyclization with the formation of products, but the yield of products obtained by intramolecular cyclization (ring formation) is rather insignificant (~5–7%).

In order to isolate initial monomers from the reaction products, the obtained copolymers were reprecipitated from the solution of dimethylformamide by hexane and dried at 80°C in vacuum till constant mass was obtained. Determination of viscosities of copolymers from 1% solution of dimethylamine showed that their intr. were within the limits of 0.25–0.60.

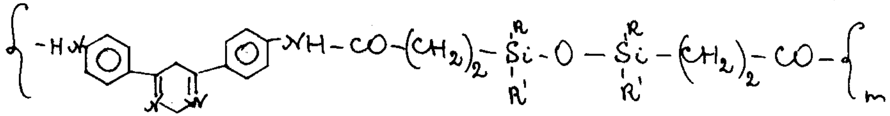
With the purpose to verify the fact that HFC reaction copolymers with regular distribution of heterocyclic fragments in the main chain are obtained, we have conducted fractionation of a copolymer III into III^1–III^3 fractions. Fractionation was carried out from dimethylformamide by hexane. Elementary analysis of these fractions slightly differ from the calculated data (Table I), certifying thus that the reaction proceeds with the formation of copolymers of regular structure.

Synthesized copolymers were identified according to the data of elementary analysis and IR spectra.

Spectra of the obtained copolymers are characterized by absorption bands of benzole ring at 730 and 1680–1590 cm^{-1}, as well as by absorption bands of NH and Si—Me links in the zone of valence fluctuation of 3220, 3450 and 1260 cm^{-1}.

TABLE II

Some physico-chemical characteristics, yields and data of elementary analysis of copolymers of the general formula



No	R	R'	n	intr of 0.5% sol. in DMFA at 20°C	Yield, %	Found, %				Formula	Calculated			
						C	H	N	Si		C	H	N	Si
VII	CH_3	CH_3	4	0.3	93	54,92	6,22	8,05	17,28	$C_{30}H_{44}Si_4N_4O_5$	55,21	6,75	8,59	17,18
VIII	CH_3	C_6H_5	4	0,31	94,6	67,01	6,13	8,38	11,98	$C_{50}H_{52}Si_4N_4O_5$	66,67	5,78	6,22	12,44
IX	CH_3	CH_3	10	0,36	91,7	46,39	7,68	5,70	26,02	$C_{42}H_{80}N_4Si_{10}O_{11}$	45,99	7,30	5,11	25,55
X	CH_3	C_6H_5	10	0.36	95,4	63,88	6,09	3,05	16,44	$C_{92}H_{100}N_4Si_{100}O_{11}$	64,34	5,83	3,26	16,32
XI	CH_3	CH_3	28	0.41	92,5	39,03	8,02	2,59	31,94	$C_{78}H_{188}N_4Si_{28}O_{29}$	38,55	7,74	2,31	32,29
XII	CH_3	C_6H_5	28	0,42	95	63,22	6,30	1,58	19,19	$C_{218}H_{244}N_4Si_{28}O_{29}$	62,82	5,86	1,34	18,83
XIII	CH_3	CH_3	100	0,5	92,6	33,62	8,45	0,63	36,51	$C_{222}H_{620}N_4Si_{100}O_{101}$	34,35	7,99	0,72	36,10
XIV	CH_3	C_6H_5	100	0,52	93,4	62,22	6,03	0,57	19,83	$C_{722}H_{820}N_4Si_{100}O_{101}$	62,08	5,86	0,4	20,06

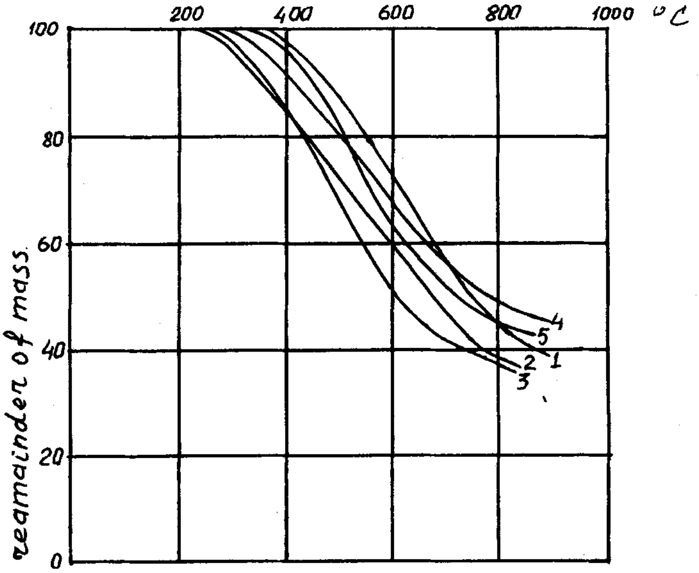
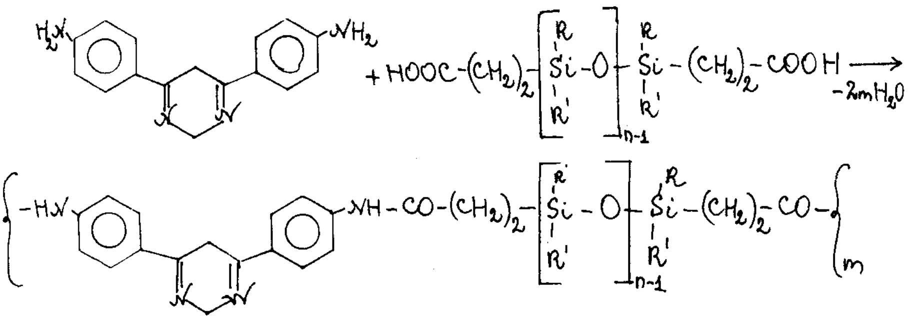


FIGURE 3 Thermogravimetric curves of copolymers: 1—for copolymer XIV; 2—for copolymer VII; 3—for copolymer X; 4—for copolymer XII; 5—for copolymer XIII; (V = 5° per min, on air).

We have also conducted thermogravimetric studies of copolymers I–VI. Figure 2 presents curves for a mass loss with respect to time, at the heating rate of 5°C per min. Copolymers started to lose mass at 300°C reaching maximum in loss at 400°C. Influence of regularly distributed siloxane fragments in a linear chain upon thermal-oxidative stability of the studied copolymers was observed. According to Figure 2, starting temperature of mass loss increases with the increase of a siloxane fragment size in copolymers. The lowest temperature was observed with the copolymer I.

In order to estimate the dependence of thermal-oxidative stability of copolymers from the sizes of siloxane fragment, temperature was selected which corresponded to 10% of mass loss of copolymers. For copolymer I, it equalled to 290°C, for a siloxane fragment consisting of 6 silicon atoms it equalled to 300°C; for a siloxane fragment with 25 silicon atoms – 400°C, and for a siloxane fragment with 100 silicon atoms – 450°C.

We have also conducted reaction of interaction of 4,6-bis(*n*-aminophenyl)pyrimidine with α,ω-bis(β-carboxylethyl)diorgano siloxanes by the method of high-temperature HFC, both without solvent, and in presence of solvent (dimethylformamide or dioxane) which proceeded as follows:



where:

$n = 4$, R = R = Me (VII), R = Me, R = Ph (VIII)
$n = 10$, R = R = Me (IX), R = Me, R = Ph (X)
$n = 28$, R = R = Me (XI), R = Me, R = Ph (XII)
$n = 100$, R = R = Me (XIII), R = Me, R = Ph (XIV)

Reaction was conducted at 150–180°C at 1:1 molar ratio of initial components. Reaction process was carried out in vacuum in order to more completely remove water released during the reaction.

Characteristics of the synthesized compounds are given in Table II.

The synthesized polymers prepared by the method of HFC are characterized by statistical distribution of rings in a polymer chain. The obtained products are soluble in DMFA, chloroform, N-methylpyrrolidone, tricresol. The solubility of the synthesized polymers undergoes changes in accordance with their composition; solubility is increased with the increase of siloxane fragment content in polymers. Copolymer, containing 100 silicon atoms is characterized by the most high solubility (Table II). It should be noted here, that at long-term standing on air, reaction products lose their dissolution capacity and that they form structurized polymers.

The above stated products are amorphous, horn-like, rubbery brown compounds.

During the process of synthesis polymers fall-out (flocculate) from the reaction medium, when the process is conducted in a solution, and the reaction of their preparation proceeds in heterogeneous system. All polymers are obtained in high yields.

With the purpose of isolating initial products, synthesized polymers were reprecipitated from the solution of dimethylformamide by hexane, and dried to their constant mass at 70°C in vacuum. Determination of viscosity data of polymers from 0.5% of dimethylformamide solution has shown, that their intrinsic viscosities are within the limits of 0.3–0.52.

The structures of the synthesized polymers were verified by elementary analysis and IR spectra.

The spectra of the obtained polymers are characterized by absorption bands of benzole ring in 730 and 1590 cm^{-1}, those of carbonyl group—in 1680 cm^{-1}, of Si—Me in 1260 cm^{-1}, of linear Si—O—Si groups in 1000–1100 cm^{-1}, and for the products VIII–X, XII, XIV absorption bands of δ_{Si-Ph} in 1460 cm^{-1}. In the process of identification, spectra of initial components were used: e.g. spectrum of initial 4,6-bis(*n*-aminophenyl)pyrimidine alongside with absorption bands of benzole ring (730 and 1590 cm^{-1}), bands of initial amino group were also observed in a zone of valence fluctuation of 3450, 3340, 3220 cm^{-1} and in a zone of deformation fluctuations δ_{NH_2} – 1650 cm^{-1}. In all spectra of copolymers these bands vanish, and only slight absorption in 3210 cm^{-1} (δ_{NH}) is observed.

Thermal-oxidative destruction of the synthesized copolymers was investigated. In Figure 3 curves of mass loss are given with respect to time, at the heating rate of 5°C per min. According to Figure 3 copolymers remain stable up to 250°C and at 280°C they lose their mass up to 5%.

Hence, interaction of 4,6-bis(*n*-aminophenyl)pyrimidine with α,ω-bis(diethylamino)- and α,ω-bis(β-carboxyethyl)diorganosiloxanes has shown, that reaction of HFC at 1:1 molar ratio of initial components, in a current of dry nitrogen, proceeds, in the main, according to the mechanism of intermolecular condensation with the formation of corresponding copolymers.

CONCLUSION

On the basis of the studies conducted by the authors, it has been established that during interaction of 4,6-bis(*n*-aminophenyl)pyrimidine with α,ω-bis(diethylamino)- and α,ω-bis(β-carboxyethyl)diorganosiloxanes, thermally stable copolymers are obtained which don't lose weight up to 300°C.

References

1. K. A. Andrianov, "Methods of elemento-organic chemistry." *Silicon*. Moscow, Nauka, 1968, p. 238 (in Russian).
2. K. A. Andrianov, I. I. Abkhazava, L. M. Khananashvili and G. D. Bagratishvili, *Zhurnal Organicheskoy Khimii*, **43**, 1505–1507 (1973) (in Russian).
3. E. D. Semenova, D. Ya. Zhinkin and K. A. Andrianov, *Izvestiya AN SSSR, ser. Khim.*, 269–271 (1962) (in Russian).