Acylation of Amino-1,2,4-triazoles

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Abstract—A scheme of acylation of amino-1,2,4-triazoles under conditions of low-temperature polycondensation is proposed. The effect of reaction conditions on the yield and properties of reaction products is established.

Regardless of conditions, polycondensation reactions are complicated and not infrequently multidirectional, as a result of interplay of a lot of variables and interrelated factors. Therefore, investigations in the field of polycondesation processes are much more descriptive than is common in the chemistry of monomers. Attempted modeling of such systems has been mentioned in [1, 2].

In such a situation growing in importance is search for empirical relationships between characteristics of the polymer formed (such as yield and molecular weight) and reaction conditions. It should be emphasized that reactions leading to polyamides of the 1,2,4-triazole series is difficult to study because of the ambident reactivity of aminotriazoles in elementary acylation (amidation) stages. Therefore, in our study on polyamidation involving dicarboxylic acid chlorides and diamines of the 1,2,4-triazole series we focussed, along with regular trends in polymer formation, on the reactivity of aminotriazoles in acylation reactions.

Oligoamides **I**–**XXXV** were prepared by known procedures [3–6].

The rigorously substantiated ability of aminotriazoles to be acylated both by exocyclic amino groups and by the ring imino group [7] is also characteristic of their reactions with acid dichlorides. The reactions of 5-amino-1,2,4-triazole with adipoyl, sebacoyl, fumaroyl, and terephthaloyl chlorides under conditions of low-temperature polycondensation in dry dimethylacetamide give low-molecular polyamides containing nonequivalent amide –(NH–CO–) and imide (N-CO) units. Such result can arise only if the reaction occurs by the following scheme: I stage: reaction between the monomers; II stage: reaction between the dimers; etc.

Alternatively, polyamides from aminotriazoles and dicarboxylic acid chlorides may by formed by diacylation of the amino group [8]. However, this scheme was proposed for the strongly basic aliphatic amines [7] and is unlikely with the weakly basic aminotriazoles.

According to speculations in [8, 9], acylation of 5-amino-1,2,4-triazole with carboxylic acid chlorides



R, R' and R" are absent (I, VIII, XV, XXII, XXIX); R = R' = NH, R" is absent (II); R = R' = NH, R' = triazol-3,5-diyl (II); R = NH, R' = CH_2 , R" = triazol-3,5-diyl (IV); R = NH, R' = $(CH_2)_2$, R" = triazol-3,5-diyl (V); R = NH, R' = $(CH_2)_4$, R" = triazol-3,5-diyl (VI); R = NH, R' = $(CH_2)_8$, R" = triazol-3,5-diyl (VII); R = NH, R' and R" are absent (IX, XVI, XXIII, XXX); R = NH, R' is absent, R" = triazol-3,5-diyl (X, XVII, XXIV, XXXI), 3-methylenetriazol-5-yl (XII, XXV, XXXII), 3-(tetramethylene)triazol-5-yl (XII, XIX, XXVII, XXXIV); Y is absent (I-VII), $(CH_2)_4$ (VIII-XIV), $(CH_2)_8$ (XV-XXI), $p-C_6H_4$ (XXIX-XXXV); n = 3-7 (I-XXXV).

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occurs initially by the ring to give 1-acyl-3(5)-amino-1,2,4-triazole. Then the acyl chloride moiety can migrate to the exocyclic amino group, yielding 3acylamino-1,2,4-triazole; therewith, the transacylation is always intramolecular [8, 10, 11]. Note that, as follows from [8, 10], the acyl migration from the ring to the exocyclic NH₂ group is favored by electronacceptor substituents R.



Our results, namely the synthesis of oligoamides under various conditions, in aqueous-alkaline solutions inclusive, suggest that aminotriazoles are not only acylated by the ring but also directly by the exocyclic amino group. Actually, if the only target for attack by the acyl group is the heteroring, i.e., as proposed in [8], the first stage of the reaction results exclusively in *N*-acyltriazole formation, then, evidently, under conditions of gas–liquid and liquid–liquid phase-transfer condensations no polymers would form at all,¹ and the reaction would involve no other processes as aminotriazole-catalyzed hydrolysis of acid chloride.



Meanwhile, it is such puttern which we observed in the gas-liquid and liquid-liquid reactions of 5-amino-1,2,4-triazole with dicarboxylic acid chlorides: Istead of expected 1,2,4-triazole polymers we obtained intractable mixtures of di- and trimers with an average molecular weight of up to 300.

The reactions of diaminotriazoles with dicarboxylic acid chlorides involve acylation of the endocyclic NH group, resulting, finally, in termination of polymeric chains in the course of synthesis or isolation of the polyamides. Here, however, a concurrent irreversible polyamidation via acylation of exocyclic amino groups takes place, and, moreover, cleavage of the azolide groups is prevented by the electron-acceptor effect of the two amino groups [13]. Under these circumstances one can expect formation of triazolecontaining oligoamides in high yields.

¹ As shown in [12], 50% of azolide groups in *N*-acetyltriazole are hydrolyzed in straight water within ~6 min, while in 0.001 N KOH solution an almost immediate hydrolysis takes place.

Thus, the oligomer formation [10, 11] in various conditions of nonequilibrium polycondensation suggests comparable probabilities of acylation by exocyclic and exocyclic amino groups. Therefore, to obtain high-molecular aminotriazoles, we should inactivate the imino group in the triazole ring by acylation and thus direct the reaction between diaminotriazoles and dicarboxylic acid chlorides exclusively on the way of amidation.

In principle, there are two possible approaches to this problem. The first involves substitution of the mobile proton of the 1,2,4-triazole ring in diaminotriazole molecules by a neutral substitutent, such as alkyl. However, this trivial approach fails with aminotriazoles: The latter tend to tautomeric transformations and thus a probability exists that the ring contains an imino group susceptible to electrophilic substitution. This is in line with our concept [13, 14] that aminoazoles in solution are present in the imino form.

The second approach is to perform the reaction in conditions favoring the target polyamidation reaction and unfavoring the side heteroring acylation reaction.

Since aminotriazoles are protonated exclusively by ring nitrogens, it was not unreasonable to suggest that in acid medium aminotriazoles would be acylated exclusively by amino groups. However, the experimental dependences of the yield of oligomers on the pH of the medium showed that the yield is sharply reduced in the absence of alkaline acceptors, while in acid medium no polyamidation takes place at all [4, 5].

Evidently, such result is explained by the fact that the electron pair of the amino group in aminotriazoles is conjugated with the π -electron system of the heteroring. Therefore, ring protonation reduces the basicity not only of ring heteroatoms but also of exocyclic amino groups, thereby reducing the reactivity of the latter toward acid chlorides [15]. Simultaneously hydrolysis and other side reactions involving acid chlorides increase in importance. This all results finally in reduced molecular weights of oligomers. However, it should be emphasized that regarless of polyamidation procedure and conditions the M_n of all the synthesized oligoamides is no higher than 2000. This value could not also be increased by using purer monomers.

The main side reaction in the polyamidation involving diaminotriazoles and dicarboxylic acid chlorides is acylation of the triazole ring, which under conditions of phase-trasfer polycondensation gives rise to hydrolysis of the acid chlorides, while in polycondensation in solution, to formation of unstable azolide units whose cleavage results in the degradation of the macromolecules into oligoamide fragments [10].



Fig. 1. Yield-temperature plots for oligoamides (1) XIV, (2) XV, (3) XXI, (4) XXII, (5) XXVIII, and (6) XXIX.

Thus, analysis of the dependences of the yield and molecular weight of the synthesized compounds on reaction conditions shows that high-molecular polyamides are principally impossible to obtain by nonequilibrium polycondensation in force of the intrinsic dual reactivity of aminotriazoles in elementary acylation acts and the presence of the imino form in solutions. The concentration of monomers in the range studied (0.01–0.30 M) has almost no effect on the yield and molecular weight (specific viscosity) of 1,2,4-triazole oligoamides. The observed insignificant variations in the yield (up to 3–4%) fall within the experimental error.

The fact that the yield of 1,2,4-triazole oligoamides is independent of monomer concentration can be explained by early chain termination. Further heating enhances mutual solubility of the aqueous and organic phases, thus enhancing hydrolysis of acid chlorides and reducing the yield and molecular weight of polymers [1]. As seen from the temperature dependences of the yield (Fig. 1), the polycondensation involving diaminotriazoles and dicarboxylic acid chlorides fits this regularity. At temperatures higher than 20°C the yield of oligoamides sharply decreases. At the same time, at reduced temperatures (5–15°C), too, slightly decreased yields are observed.

It should be noted that the temperature-yield curves for the gas-phase and liquid-phase polyamidations have different shapes. In the gas-liquid system, the yield increases with temperature, while in the liquid-liquid system, a smooth maximum is observed at about 20°C. Such difference was first observed in [1, 15] in the synthesis of polyhexamethyleneoxamide and explained by different temperature effects on the mutual solubility of the phases and thus on the degree of hydrolysis of acid chlorides.



Fig. 2. Yield-monomer ratio plots for oligoamides XV, XXII, and XXIX. $c_{\text{diamine}}^0 = \text{const.}$



Fig. 3. Yield–pH plots for oligoamides **XV**, **XXII**, and **XXIX** ($c_{\text{diamine}}^0 = c_{\text{acid dichloride}}^0$ 0.05 M, reaction temperature 20°C).

Phase-transfer polycondensation of diamines with dicarboxylic acid chlorides is most commonly almost insensitive to monomer ratio, since the rate of the main reaction (polyamidation) is very high and limited by diffusion of the reagents from bulk phases to their interface, i.e. into the reaction zone [1].

The effect of monomer ratio on the synthesis of oligoamides we studied by varying the initial concentration of acid chlorides at constant initial concentrations of diamines and HCl acceptor. The resulting experimental data are given in Table 2. Our data are analogous to published data [1].

In view of the fact that the pH of the medium can differently affect condesation polyamidation processes, we studied the effect of acid–base properties of the medium of the yield and molecular weight of oligo-amides. The pH of the aqueous phase was varied by adding hydrochloric acid or sodium hydroxide. The resulting data are represented in Fig. 3.

The experimental data show that the reactions of diaminotriazoles and adipoyl chloride yield polymeric products only in the presence of HCl acceptor (NaOH); therewith, the highest yield is attained at a 2:1 NaOH: diamine molar ratio in the aqueous phase, in agreement with published data [1, 16, 17]. The the molecular weight (specific viscosity) of oligoamides proved invariable within error, i.e., independent of the pH of the aqueous phase.

For successful polycondensation in solution, two conditions should be met. First, starting monomers should be soluble in the solvent to be used and, second, there should be almost no reactions between the solvent and the starting reagents. In all syntheses we applied the same reagent mixing scheme, when a solid or a liquid acid dichloride was added with stirring in one portion to a solution of diamine in dimethylacetamide. As shown in [16, 18], thus one prevents side reactions between the dichloride and the solvent. The stirrer speed in the range studied (1000-15000 rpm) has almost no yield effect. At the same time, at higher stirrer speeds overheating and foaming of the reaction mixture was observed, and, therefore, further work was performed at a stirrer speed of 1000 rpm.

Polycondensation of diamines with acid dichlorides in solution is usually complete in 1 h. But the reaction time may range from several minute to several hours, depending on conditions [16, 19, 20]. The conversion increases with increasing monomer concentrations. The highest yield is observed in a wide range of concentrations (0.2-1.0 M). The reduced yield at concentrations below 0.2 M is apparently explained by increase in the relative concentration of admixtures and the resulting acceleration of side reactions. The reduced yield at monomer concentrations above 1.0 M is explained by increased viscosity of the system. The wider optimum concentration range for the system in study compared with systems described in the literature is associated with better solubilities of the monomers and oligomers in the solvent applied. The highest yield of oligoamides is at monomer concentrations of 0.5 M (95%), but in further experiments we used monomer concentrations of 0.2 M, providing an almost the same yield (93%).

Experiments with 3,5-diamino-1,2,4-triazole and adipoyl and terephthaloyl chlorides showed that the main reaction (polyamidation) is only slightly decelerated at lower temperatures in view of the higher activity of terephthaloyl chloride and the higher catalytic activity of the solvent (DMAA). Therewith, side reactions are still more decelerated. The freezing point of DMAA is -20° C. Therefore, there is little point in performing the reactions below this temperature because of the increased viscosity of the system. Moreover, low temperatures are rather difficult to maintain under conditions of exothermal reaction. In view of the acceleration of side reactions, temperatures above 30°C, too, are unsuitable. Figure 4 depicts the temperature-yield plots for oligoamides **XV**, **XXII**, and **XXIX**.

The fact that the yield of oligoamides decreases with increasing temperature can be related to increasing contribution of side reactions, primarily the reaction of the dichlorides with DMAA. The range of monomer concentrations suitable for synthesis of compounds **XV**, **XXII**, and **XXIX** proved rather narrow (0.5–0.1 M) because of the poor solubility of diamines in DMAA.

Abundant evidence [15, 18] shows that the maximum M and the maximum yield of polyamides are attained at equimolar monomer ratios. As follows from our results, this is also true of the system in study. The corresponding experiments were performed at 18°C with the concentration 0.2 M. The resulting yield–monomer ratio plot is given in Fig. 5.

The unsymmetrical shape of the plots suggests that hydrolysis of acid chlorides occurs at a higher rate than salt formation by amino groups. Mention has been made in the literature of the suppression the hydrolysis in the presence of a small excess of acid chloride. However, in our case this approach proved ineffective.

Thus, by examining the effect of reaction conditions on the yield of oligoamides we found the following optimal conditions of the synthesis: monomer concentration 0.2 M, temperature 18°C, and equimolar monomer ratio.

The unsymmetrical shapes of the curves in Fig. 5 are apparently explained by the different nature of side reactions that occur when one or the other monomer is in excess. With excess acid dichloride, transacylation and transamination reactions involving the dichloride–DMAA complex are much enhanced. With excess diamine, no destructive reactions are initiated, and the yield of polymers is reduced by no other reason than disturbed equimolarity of the reagents. Moreover, the excess of diamine is partly compensated for by salt formation during the reaction (diamine plays the role of HCl acceptor).

EXPERIMENTAL

The IR spectra (Table 1) were obtained on an IKS-29 spectrophotometer for suspensions in fluorinated



Fig. 4. Yield–initial temperature plots for oligoamides XV, XXII, and XXIX.



Fig. 5. Yield–monomer ratio plots for oligoamides XV, XXII, and XXIX. *c* 0.2 M, reaction temperature 18°C.

or Vaseline oils (solid samples) or thin films between KBr plates (liquid samples). For measurements in the 4000–400 cm⁻¹, KBr glasses were used. The ¹H NMR spectra were measured on a Bruker WP-80 spectrometer in DMSO- d_6 (80 MHz, internal reference TMS).

Physicochemical properties of the oligomers and details of their synthesis are listed in Tables 2 and 3.

N,*N*-Dimethylacetamide was kept for 24 h (with intermittent shaking) over P_2O_5 and then distilled at atmospheric pressure over fresh portions (50 g per 1 l) of P_2O_5 . For synthesis was used a fraction with bp 166–167°C (760 mm) (bp 165°C [4]). Moisture content (by Fisher) 0.05%.

Comp. no.	v(NH)	СО	Stretching vibrations of the triazole ring	Other vibrations			
I	2950 m, 2730 w, br 2334 w, br	1663 s	1550 w, 1500 br, 1485 v.s, 1405 v.s, 255 s	_			
III	2335 w, br, 2985 w, br, 2890 m, br, 2970 m, br	1665 s	1580 br, 1530 w, 1485 v.s, 1395 v.s, 1275 br, 1350 s, 1270 m	2930 w [v(CH ₂)], 1470 br [δ (CH ₂)]			
VIII X	2720 m, br 2963 w, 2360 m, br	1660 s 1680 s	1562 w, 1517 m, 1485 s, 1400 s, 1270 m 1575 w, 1505 m, 1480 v.s, 1400 s, 1290 v.s	2860 w, 745 w 2932 m[v(CH ₂)], 2860 w, 1465 m [δ(CH ₂)], 745 w			
XII	2960 w, 2880 br	1670 s	1610 s, 1565 s, 1545 br, 1490 br, 1480 v.s, 1425 m, 1385 m, 1350 s, 1300 br	2930 m[v(CH ₂)], 2855 w, 1460 w [δ (CH ₂)], 733 w			
XIV	2955 w, 2735 w, br	1665 s	1553 w, 1508 m, 1475 s, 1395 s, 1305 m	2935 w [v(CH ₂)], 2865 w, 1463 br $[\delta(CH_2)]$, 737 w			
XVI	2973 w, 2420 w	1650 s	1577 w, 1507 m, 1483 v.s, 1400 s, 1292 v.s	2927 w [v(CH ₂)], 2863 w, 1470 m [δ(CH ₂)], 755 w			
XVIII	2830 w, 2465 m, br	1673 s	1607 m, 1560 m, br, 1487 br, 1480 v.s 1385 m, 1375 v.s, 1295 w, 1292 v.s	2940 m[v(CH ₂)], 2865 w, 1465 m [δ (CH ₂)], 747 m			
XX	2885 w, 2385 w	1680 s	1575 w, 1523 w, 1485 v.s, 1400 br, 1395 m, 1270 m	3127 w [v(CH ₂)], 1165 m, br $[\delta(CH_2)]$			
XXII	2900 w, 2405 w	1670 s	1590 m, 1553 m, 1522 w, 1485 v.s., 1410 m, 1390 s, 1303 br, 1260 m	3123 w [v(CH ₂)], 2942 m[v(CH ₂)], 2865 w, 1463 m[δ(CH ₂)], 1168 w [δ(CH ₂)], 737 w			
XXIX	2960 w, 2358 w, br	1645 s	1565 w, 1505 br, 1485 v.s, 1395 v.s, 1272 w	1120 m, 1030 w, 990 w $[\delta(C_6H_4)]$			
XXXI	2940 w, br, 2370 w, br	1660 s	1610 w, 1580 br, 1530 w, 1520 w, 1485 v.s, 1430 m, 1395 v.s, 1350 s, 1275 m, 1270 m	1122 m, 1035 m, br, 993 w $[\delta(C_6H_4)]$			
XXXIII	2455 w, br		1608 m, 1602 br, 1560 m, 1483 s, 1437 m, 1385 s, 1352 w, 1305 br, 1268 w	1130 w, 1020 w, 985 w, br $[\delta(C_6H_4)]$			

Table 1. IR absorption bands of 1,2,4-triazole oligoamides (cm⁻¹)

Table 2. Physicochemical properties and elemental analyses of oligoamides

Comp. no.	Method of syn- thesis ^a	η _{sp} , ^b dl/g	ρ, kg/m ³	T _{VDO} , ^c °C	Found, %			Elementary	Calculation, %			м
					С	Н	N	formula	С	Н	Ν	11/1
I	G	0.04	1395	230	30.4	2.3	43.8	C ₄ H ₂ N ₄ O ₂	31.4	2.0	45.7	1020
III	G	0.04	1422	255	31.8	2.2	49.4	$C_6H_5N_9O_2$	32.7	1.8	50.9	970
Χ	PT	0.04	1480	290	_	_	_	0 5 7 2				
XVI	S	0.04	1421	280	50.1	6.4	32.2	$C_{12}H_{19}N_5O_2$	50.6	6.1	33.7	1260
	PT	0.03	1361	265	_	_	_	12 17 0 2				
XX	S	0.05	1405	270	_	_	_					
	PT	0.06	1370	255	53.6	7.5	25.2	$C_{17}H_{24}N_8O_2$	54.3	7.2	26.4	1880
XXIX	PT	0.04	_	250	57.7	8.5	24.0	$C_{10}HN_4O_9$	59.4	8.2	25.2	_
XXXIII	PT	0.02	1511	275	37.5	2.8	44.1	$C_{16}H_{15}N_7O_2$	39.0	2.5	45.5	_

^a Here and in Table 3: (G) gas-phase, (PT) phase-transfer, and (S) solution. ^b Specific viscosity. ^c Vigorous decomposition onset point.

N,N-Dimethylacetamide + LiCl was supplied by VNIIV Proekt (St. Peterburg). Moisture content (by Fisher) 0.10 %.

5-Amino-1,2,4-triazole was prepared by the procedure in [21] by thermal cyclization of formylaminoguanidine formed by heating a mixture of aminoguanidine bicarbonate and aminoformic acid. Purification was performed by triple crystallization from absolute ethanol, followed by drying at 80°C (1 mm) for 24 h. Colorless powder.

3,5-Diamino-1,2,4-triazole was synthesized by the procedure in [18] from dicyandiamide and hydrazine hydrate. For purification the product was doubly crystallized from 95% ethanol and dried at 80°C (1 mm) for 24 h. Colorless crystals. Analytical characteristics of the sample were consistent with published data [18].

Bis-3,3'-(5-amino-1,2,4-triazolyl) [22] was prepared by base cyclization of oxalylaminoguanidine synthesized by refluxing aminoguanidine hydrochloride and oxalic acid in water. For purification the reaction products were dissolved in conc. H_2SO_4 and reprecipitated from a fivefold volume of ice water. The precipitate was filtered off, and the procedure was repeated. After that the product was reprecipitated from 15% aqueous alkali by addition of 5% HCl to neutral reaction. The product was thoroughly washed with distilled water and acetone, and dried at 80–90°C (1 mm) for 24 h. Colorless powder.

Bis-3,3'-(5-amino-1,2,4-triazolyl)methane was synthesized from aminoguanidine hydrochloride and malonic acid [22]. After triple crystallization from water (with charcoal) is was dried at 80–90°C for 24 h. Colorless powder.

Table 3. Conditions of synthesis of 1,2,4-triazole oligoamides I-XXXV

Comp. no.	Method	Reaction medium	Quantity of more	nomers, g (mol)	Acceptor of	Stirring speed, rpm	Reaction tempera- ture, °C	Reaction time, rpm	Yield, %
			diamine	acid chloride	HCl (mol)				
I	G	Water	14.87 (0.15)	19.04 (0.15)	NaOH (0.30)		98±1	10-11	52
I	G	"	4.98 (0.03)	3.81 (0.03)	NaOH (0.60)	_	98±1	3-4	31
III	G	"	5.41 (0.03)	3.81 (0.03)	NaOH	_	98±1	3-4	23
IV	G	"	6.67	3.81	NaOH	_	98±1	3–4	20
V	G	"	8.35 (0.03)	3.81 (0.03)	NaOH (0.60)	_	98±1	3–4	21
VI	G		5.77 (0.03)	3.81 (0.03)	NaOH (0.60)	_	98±1	3–4	15
VII	S	DMAA	5.05 (0.06)	10.98 (0.06)		2000	20	30	65
VIII	S	DMAA + LiCl	5.95 (0.06)	10.98 (0.06)	_	2000	20	30	73
IX	РТ	Water– hexane	2.97 (0.03)	7.32 (0.04)	NaOH (0.04)	10000	20	5	70
Χ	РТ	"	1.66 (0.01)	2.01 (0.011)	NaOH (0.11)	7000	20	5	65
XI	S	DMAA + LiCl	5.41 (0.03)	5.49 (0.03)		2000	20	30	75
XII	РТ	Water– hexane	1.80 (0.01)	2.01 (0.011)	NaOH	7000	20	5	72
XIII	S	DMAA + LiCl	6.67 (0.03)	5.49 (0.03)	_	2000	20	30	71
XIV	РТ	Water– hexane	2.22 (0.01)	2.01 (0.011)	NaOH (0.11)	2000	20	5	69
XV	S	DMAA + LiCl	8.35 (0.03)	5.49 (0.03)	_	2000	30	30	74
XVI	РТ	Water– hexane	2.78 (0.01)	2.01 (0.011)	NaOH (0.11)	7000	20	5	72
XVII	РТ		1.92 (0.01)	2.01 (0.011)	NaOH (0.11)	7000	20	5	61
XVIII	S	DMAA	5.05 (0.06)	14.35 (0.06)	_	2000	20	30	73
XIX	S	DMAA + LiCl	5.95 (0.06)	14.35 (0.06)	_	2000	20	30	75

Comp. no.	Method	Reaction medium	Quntity of mon	omers, g (mol)	Acceptor of	Stirring speed, rpm	Reaction tempera- ture, °C	Reaction time, rpm	Yield
			diamine	acid chloride	HCl (mol)				
XX	PT	Water– hexane	0.99 (0.01)	2.39 (0.01)	NaOH (0.10)	10000	20	5	71
XXI	PT	"	1.66 (0.01)	2.39 (0.01)	NaOH (0.10)	10000	20	5	68
XXII	S	DMAA + LiCl	5.41 (0.03)	7.17 (0.03)	—	2000	30	30	77
XXIII	РТ	Water– hexane	1.80 (0.01)	2.39 (0.01)	NaOH (0.10)	7000	20	5	76
XXIV	S	DMAA + LiCl	6.67 (0.03)	7.17 (0.03)	—	2000	30	30	77
XXV	РТ	Water– hexane	2.78 (0.01)	2.39 (0.01)	NaOH (0.10)	7000	20	5	78
XXVI	PT	"	1.92 (0.01)	2.39 (0.01)	NaOH (0.10)	7000	20	5	71
XXVII	S	DMAA + LiCl	5.95 (0.06)	9.30 (0.06)	_	2000	5–10	30	76
XXVIII	S	DMAA + LiCl	5.95 (0.06)	9.30 (0.06)	—	2000	20	30	72
XXIX	РТ	Water– hexane	0.99 (0.01)	1.55 (0.01)	NaOH (0.10)	7000	20	5	72
XXX	PT	"	1.66 (0.01)	1.55 (0.01)	NaOH (0.10)	7000	20	5	60
XXXI	S	DMAA + LiCl	5.41 (0.03)	4.65 (0.03)	_	2000	30	30	72
XXXII	РТ	Water– hexane	1.80 (0.01)	1.55 (0.01)	NaOH (0.10)	7000	20	5	70
XXXIII	PT	"	2.22 (0.01)	1.55 (0.01)	NaOH (0.10)	7000	20	5	70
XXXIV	S	DMAA + LiCl	8.35 (0.03)	4.65 (0.03)	_	2000	30	30	74
XXXV	PT	Water– hexane	1.92 (0.01)	1.55 (0.01)	NaOH	7000	20	5	68

Table 3. (Contd.)

1,7-Bis(5-amino-1,2,4-triazol-3-yl)octane [22] was obtained from aminoguanidine hydrochloride and sebacic acid. Purification was performed by triple crystallization from boiling water, followed by washing with water and acetone, and 24-h drying at 80°C (1 mm). Colorless crystals. All analytical characteristics of the sample are close to thos reported in [22].

5-Amino-1*H***-1,2,3,4-tetrazole** was obtained as described in [23]. Colorless crystals. After crystallization from water (1:4) and drying in air the yield was 121 g (65%), mp 205.5–206.5°C (mp 206.5–207.5°C [22]).

Oxalyl chloride was synthesized by the Staudinger method [24] by treatment of excess phosphorus pentachloride with anhydrous oxalic acid. Purification was performed by quintuple distillation at atmospheric pressure, collecting a fraction with bp 61.0–61.1°C (735 mm) (bp 61°C [25]). Yield 10–12%.

Adipoyl chloride. A commercial reagent of pure grade was purified by triple vacuum distillation, collecting a fraction with bp 100–101°C (2 mm) {bp 126°C (12 mm) [26]}. Yield 15–20%. The distillation should be rapid and in small portions (50 ml) to avoid strong tarring.

Sebacoyl chloride. A commercial reagent of chemically pure grade was purified by triple distillation at reduced pressure collecting a fraction with bp 150–152°C (3–4 mm) {bp 142°C (2 mm) [27]}.

Fumaroyl chloride was prepared by refluxing fumaric acid in excess thionyl chloride [28] and purified by distillation on a packed column 15 cm in

height, collecting a fraction with bp 58–58.4°C (36 mm) {bp 59°C (16 mm) [25]}.

Terephthaloyl chloride. A commercial reagent of pure grade was recrystallized from dry hexane and distilled at reduced pressure, collecting a fraction with bp $112-114^{\circ}C$ (5 mm). The resulting sample melted at $83-84^{\circ}C$ (mp $83-84^{\circ}C$ [25]).

The purified acid chlorides were sealed in ampules and stored in the dark. Terephthaloyl chloride was stored in tightly stopped polyethylene beakers in a vacuum dessicator. Adipoyl chloride and fumaroyl chloride were unstable and tarred on storing; therefore, they were purified immediately before use. The other acid chlorides could be stored under the above conditions for some months.

Phase-transfer polycondensation in a gas–liquid system. Diamine, 0.03 mol, and 0.06 mol of sodium hydroxide were dissolved in 100 ml of water. The resulting solution was heated in a beaker equipped with a temperature-control unit and placed in a salt bath to a specified temperature (usually $90\pm1^{\circ}C$), a thin-wall evaporator with 0.03 mol of oxalyl chloride was placed into the beaker. Oxalyl chloride vapors was barboted by means of a gas-outlet tube through the solution for 3–4 min, after which heating was discontinued, and the reaction mixture was allowed to cool to room temperature. The resulting oligoamide that precipitated as colored flakes was filtered off and washed with water (to remove Cl⁻ ions) and acetone.

To remove unreacted monomers and other low-molecular admixtures, the oligomers were heated under reflux in 100 ml of 50% aqueous acetone for 3 h. The precipitate was then filtered off, washed with acetone and ether, and dried at 80° C (1–2 mm) for 12 h.

Phase-transfer polycondensation in a liquid– **liquid system.** A solution of 0.01 mol of diamine and 0.02 mol of sodium hydroxide in 200 ml of water and a solution of 0.01 mol of acid chloride in 200 ml of dry hexane were placed one after another in a homogenizer, after which a stirrer and a timer were started simultaneously. The stirring time was 5 min at $7000 \pm$ 100 rpm. After that the reaction mixture (a colored emulsion or a gel) was separated by centrifugation on an MPW-2 centrifuge (3–5 min at ~5000 rpm). Further workup was performed as described above.

Polycondensation in solution. A solution of 0.03 mol of diamine in 300 ml of *N*,*N*-dimethylacetamide doped with 3% of LiCl were placed in a homogenizer, after which 0.03 mol of acid chloride was added rapidly, and a stirrer and a timer were started simultaneously. Stirring $(2000\pm50 \text{ rpm})$, by a tachometer) was continued for 30 min, during which time the reaction mixture turned a brightly colored solution. The resulting oligoamides were isolated in two ways.

a. The reaction mixture was slowly poured with vigorous stirring into 1 l of cold water. Stirring was continued for 10–15 min, and the resulting oligoamide that precipitated as flakes was separated by centrifuging on an MP-2 centrifuge. The centrifugation time was 3-5 min at ~5000 rpm.

b. The reaction mixture was slowly poured with vigorous stirring into 300 ml of dry acetone. Stirring was continued for 10–15 min. The precipitate that formed was filtered off and treated with dry acetone in a Soxhlet apparatus for 3–4 h to remove the starting monomers and other admixtures. The oligomer was filtered off, washed with dry acetone, and vacuum-dried at 80°C (1–2 mm) for 12 h.

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