

Nylon 7, A Fiber Forming Polyamide*

C. F. HORN, B. T. FREURE, H. VINEYARD, and H. J. DECKER,
*Research Department, Union Carbide Chemicals Company,
South Charleston, West Virginia*

Nylon 7, the polyamide from 7-aminoheptanoic acid, was discovered by coincidence by Manasse in 1902¹ who obtained the multiple of $C_7H_{13}NO-NH(CH_2)_6CO-$ when heating 7-aminoheptanoic acid to determine its melting point. Although, based on the fundamental work on polyamides by Carothers,² polyamide fibers such as nylon 6 (polycapromide) and nylon 66 (polyhexamethyleneadipamide) experienced a worldwide growth during the past twenty years, relatively little became known about nylon 7 (polyheptanamide). Laboratory samples of nylon 7 were prepared by academic routes, e.g., suberone \rightarrow suberoneoxime \rightarrow enantholactam;³ pimelonitrile \rightarrow 7-aminoheptanonitrile \rightarrow 7-aminoheptanoic acid,⁴ and a few properties of the polyamide were determined. Wiloth⁵ conducted kinetic measurements on the polycondensation of 7-aminoheptanoic acid, and Schaaf⁶ studied the polymerization of the enantholactam. During the past few years, however, a group of Russian researchers⁷ developed a process for 7-aminoheptanoic acid via telomerization of ethylene with carbon tetrachloride to the 1,1,1,7-tetrachloroheptane and its subsequent hydrolysis and amination. The development of a nylon 7 fiber based on this monomer synthesis has been reported to be under study.

An industrially feasible synthesis for ethyl-7-aminoheptanoate, a monomer for nylon 7, and a simple polycondensation process to the high molecular weight polyamide were developed in this laboratory. Moreover, a detailed study of the fiber properties of this polymer was carried out.

PREPARATION OF ESTERS OF 7-AMINOHEPTANOIC ACID

The starting material for the synthesis of esters of 7-aminoheptanoic acid is ϵ -caprolactone which can readily be prepared by oxidation of cyclohexanone with peracetic acid as described by Starcher and Phillips.⁸ A total of eight esters of 7-aminoheptanoic acid were prepared in excellent yield by a four-step process which is shown in Table I.

The stability of these esters against polymer formation during distillation and at room temperature is shown in Table II.

* Presented before the Division of Polymer Chemistry, 139th Meeting of the American Chemical Society, St. Louis, March 1961.

TABLE I
Synthesis of Esters of 7-Aminoheptanoic Acid

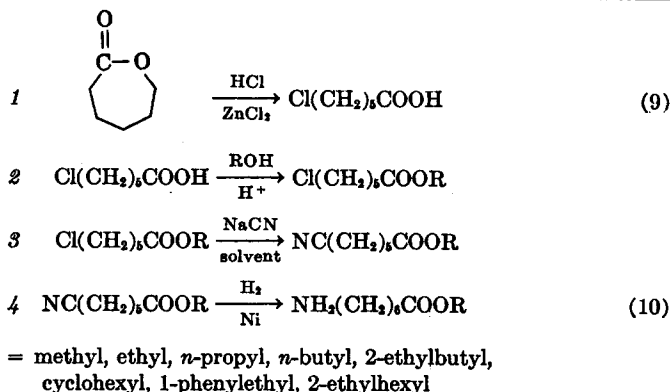


TABLE II
Esters of 7-Aminoheptanoic Acid and Their Stability Against Polymer Formation

Ester	Boiling temp., °C., mm. Hg	Refractive index, n_D^{20}	Stability ^a during distillation	Stability ^b at 20°C.
Methyl	70/1	—	33	< 1 h
Ethyl	78–81/1	1.4368	5–7	1–1.5 d
<i>n</i> -Propyl	78–80/0.5	n.d. ^c	5	2 d
<i>n</i> -Butyl	85–90/0.4	1.4396	0.5	7 d
2-Ethylbutyl	104–106/0.4	1.4442	n.d.	6 d
Cyclohexyl	110–115/0.5	n.d.	4.5	8 d
1-Phenylethyl	145–155/0.4	1.4976	20	6 d
2-Ethylhexyl	residue product	n.d.	n.d.	10 d

^a Loss of ester during distillation due to polymer formation.

^b Hours (h) or days (d) of storage before formation of polymeric precipitate occurred.

^c Not determined.

The precipitate formed at room temperature during the stability test was a linear oligomeric product consisting of not more than 5 repeating units. The low molecular weight is probably due to the fact that after the oligomers have reached a certain chain length they become insoluble in the monomeric ester and crystallize out. The formation of the alcohol which parallels the oligomerization adds to the insolubility of the product. In the absence of water the formation of the low molecular weight polymer is believed to be due to aminolysis. The rate of aminolysis appears to decrease with the increase in the number of carbon atoms in the alcohol.

The polymer residues obtained during the distillation of the esters ranged in reduced viscosity between 0.1 and 0.35 [$I_R = (\Delta N/N_o)(1/C)$; $C = 0.2$ g./100 cc. solution; solvent: phenol-tetrachloroethane (3:2); tempera-

ture: 30°C.]. They can be reconverted to the ester by alcoholysis under superatmospheric pressure.

PREPARATION OF NYLON 7

When the esters of 7-aminoheptanoic acid were heated at 270°C. for several hours at atmospheric pressure to bring about their polycondensation into a high molecular weight polyamide, the same trend in stability of the esters as shown during the distillation and at room temperature (Table II) was observed. During the heating a stream of nitrogen was passed through the melt to facilitate the removal of the corresponding alcohol. The polymers obtained from esters with higher or secondary alcohols were of lower molecular weight than those from esters with lower primary alcohols.

TABLE III
Preparation of Nylon 7 from Esters of 7-Aminoheptanoic Acid
 $n\text{NH}_2(\text{CH}_2)_6\text{COOR} \rightarrow \text{—NH}(\text{CH}_2)_6\text{CO—}_n + n\text{ROH}$

Ester	Polycondensation		I_R
	Time, hr.	Temp., °C.	
Methyl*	5	270	0.89
Ethyl	4	270	0.66
<i>n</i> -Propyl	3.5	270	0.76
<i>n</i> -Butyl	5	270	0.48
2-Ethylbutyl	5	270	0.38
Cyclohexyl	5	270	0.36
1-Phenylethyl	5.5	270	0.55
7-Aminoheptanoic acid	1.5	270	1.64

* Methyl ester was essentially oligomeric before heating.

It was surprising that the methyl and ethyl esters, which readily formed oligomeric products at room temperature, did not produce higher molecular weight polymers upon heating than those listed in Table III, while the amino acid reached a reduced viscosity of about twice as high in less than one-third of the time. Even heating the ethyl ester as long as 16 hr. did not yield a polyamide of sufficient molecular weight for melt extrusion (I_R 1.0 to 1.9). Only after about 24 hr. at 270°C. was a polyamide having a reduced viscosity of 1.15 obtained which, however, was discolored due to some thermal decomposition.

The difference in polycondensation rate between the amino acid and its esters is in agreement with the postulation that the polycondensation of the amino acid is autocatalyzed by H^+ ions from the carboxyl groups.⁵ In the absence of H^+ ions in the esters the polycondensation is believed to be based on an aminolytic reaction influenced by steric conditions of the ester groups. The addition of such materials as CaCO_3 , LiAlH_4 , CH_3ONa , and

NaOH to the ethyl ester did not have any catalytic effect upon the ester condensation.

The ethyl ester was heated with deionized water at 90–100°C. for a few hours at atmospheric pressure. After removing the water and some of the alcohol formed during the heating period, a product was obtained which could readily be converted into high molecular weight nylon 7.¹¹

The product, hereafter called precursor, isolated after the initial heating period is a white, waxy to brittle solid at room temperature which melts between about 140 and 180°C. (m.p. of aminoheptanoic acid 195°C.), depending somewhat upon the maximum heating temperature as well as upon the amount of water used. The precursor is stable at room temperature and can be stored and handled without special precautions. Molecular weight determination of the precursor indicated that it is essentially of monomeric and to a lesser degree of dimeric nature. Although no conclusive evidence was found, it appears to be likely that trace amounts of enantholactam and higher linear oligomers are also formed, particularly higher temperatures. The infrared spectrum of the precursor showed strong bands at 6.6 and 7.2 μ for $-\text{COO}^-$, at 3.2 μ for $-\text{NH}_3^+$, and at 6.1 μ for $-\text{NH}_2$ and $-\text{NHCO}-$. The band at 5.8 μ can probably be attributed to $-\text{COOH}$ and $-\text{COOC}_2\text{H}_5$ as well. Typical for some amino acids, the bands at 3.9 and 4.7 μ were also present. The characteristics of the precursor suggest the reactions shown in Table V during the initial heating period.

Table V shows that reactions 1 and 6 (hydrolysis) dominate 2 and 3 (aminolysis) as more water is used in the initial heating period. Reactions 4 and 5 (amidation) are possible during the removal of the water-ethanol mixture at temperatures of 100°C. or higher. Thus, it was concluded that

TABLE IV
Polycondensation of Ethyl-7-Aminoheptanoate in Presence of Water (Correlation between mole ratio ester:water and molecular weight of polyamide)

Mole ratio ester to water	Heating with water		Polycondensation		I_R
	Time, hr.	Temp., °C.	Time, hr.	Temp., °C.	
1	0.1	3.5	4	270	0.66
1	1	3	4	270	0.72
1	1.5	3	4	270	0.64
1	2	3	4	270	0.70
1	3	3	4	270	1.00
1	4	3	4	270	1.02
1	5	3	4	270	1.18
1	10	3	3.75	270	1.70
1	15	3	4	270	2.05
1	20	3	4	270	2.01
1	—	—	4	270	0.66
1	—	—	24	270	1.15

TABLE V
Possible Reactions during Initial Heating Period of Ester with Water

1	$\text{NH}_2\text{-R-COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_2\text{-R-COOH} + \text{C}_2\text{H}_5\text{OH}$
2	$\text{NH}_2\text{-R-COOC}_2\text{H}_5 + \text{NH}_2\text{-R-COOC}_2\text{H}_5 \rightleftharpoons \text{NH}_2\text{-R-CONH-R-COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH}$
3	$\text{NH}_2\text{-R-COOC}_2\text{H}_5 + \text{NH}_2\text{-R-COOH} \rightleftharpoons \text{NH}_2\text{-R-CONH-R-COOH} + \text{C}_2\text{H}_5\text{OH}$
4	$\text{NH}_2\text{-R-COOH} + \text{NH}_2\text{-R-COOC}_2\text{H}_5 \rightleftharpoons \text{NH}_2\text{-R-CONH-R-COOC}_2\text{H}_5 + \text{H}_2\text{O}$
5	$\text{NH}_2\text{-R-COOH} + \text{NH}_2\text{-R-COOH} \rightleftharpoons \text{NH}_2\text{-R-CONH-R-COOH} + \text{H}_2\text{O}$
6	$\text{NH}_2\text{-R-CONH-R-COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_2\text{-R-CONH-R-COOH} + \text{C}_2\text{H}_5\text{OH}$

$\text{R} = \text{-(CH}_2\text{)}_6\text{-}$

the precursor is a mixture of 7-aminoheptanoic acid with mainly dimeric acid and ester. Ammonium salt formation between these three components is suggested by the infrared spectrum.

In most cases no isolation of the precursor is required and the polycondensation is brought about by simply raising the temperature to about 270°C. to distill out water and ethanol (see Table IV). If the precursor is isolated, however, it can readily be converted into high molecular weight nylon 7 by heating at atmospheric pressure as shown in Table VI.

Although the available experimental data do not suffice for the postulation of the chemical mechanism of the polycondensation reaction, they point towards a H^+ ion catalyzed process whereby the H^+ ions are probably furnished by the -COOH groups present in the precursor.

Water and methanol extractions of the high molecular weight nylon 7 yielded about 1.5% extractable material which appeared to be of oligomeric nature. Its infrared spectrum was essentially identical with that of high molecular weight nylon 7. The product was insoluble in dilute caustic.

FIBER PROPERTIES OF NYLON 7

Nylon 7 is a semi-crystalline, white polyamide, which, to be useful as a fiber, film, or molding resin, should have a molecular weight between about 15,000 and 30,000. It is thermostable above its melting point of 225°C. in an inert atmosphere up to 300°C. and can be kept in the molten state at 250°C. for at least 24 hr. without indications of decomposition. Its resistance to basic as well as acidic reagents, organic solvents, and oxidizing agents is comparable to that of nylon 66. In addition to the melting point, three transition temperatures were determined with a torsional pendulum at -130, -70, and +50°C. Some of its physical properties are summarized in Table VII, permitting a comparison with those of other polyamides from ω -amino acids.

While moisture regain and density are mainly influenced by the total number of $\text{-CH}_2\text{-}$ groups per repeating unit, the melting points are dominated by the extent of hydrogen bonding between the parallel and

TABLE VI
Preparation of Nylon 7 from the Precursor^a
precursor $\xrightarrow[\text{N}_2]{270^\circ\text{C.}}$ $-\text{NH}(\text{CH}_2)_6\text{CO}-_y + x\text{H}_2\text{O} + z\text{C}_2\text{H}_5\text{OH}$

Polycondensation ^b		
Time, hr.	Temp., °C.	I_R
0.5	270	1.1
1	270	1.5
1.5	270	1.73
2	270	1.92
3	270	2.11

^a Precursor was prepared by heating a mixture of ethyl-7-amino-heptanoate and water (mole ratio 1:9) for 3 hr. at 110°C. under reflux and subsequent removal of water and ethanol by distillation between 100 and 105°C.

^b A stream of nitrogen was passed through the melt.

TABLE VII
Physical Properties of Polyamides from ω -Amino Acids

Polyamide	$-\text{NH}-$ $(\text{CH}_2)_n\text{CO}-$	M.p., °C.	Moisture ^a regain, %	Density ^b	Sticking temp., °C.
Nylon 6	$n = 5$	214	4.7	1.14	208
Nylon 7	$n = 6$	225	2.6	1.10	220
Nylon 8	$n = 7$	185	1.8	1.08	181
Nylon 9	$n = 8$	194	1.45	1.06	190
Nylon 10	$n = 9$	177	1.25	1.04	172
Nylon 11	$n = 10$	182	1.2	1.04	173

^a At 20°C. and 65% relative humidity.

^b Of highly crystalline polymer.

TABLE VIII
Textile Properties of Nylons 7, 6, and 66

	Nylon 7 (250/30)	Nylon 6 (840/140)	Nylon 66 (210/34)
Tenacity, g/d.	7.4-7.8	7.3-7.8	7.5-8.0
Elongation, %	14.0-16.0	24.0	18.0
Stiffness, g/d. ^a	42-45	38	50
Shrinkage, % in			
boiling water	8.0-10.0	12.0	10.0
150°C. air	8.5-11.0	11.0	8.0
200°C. air	11.0-13.0	15.0	11.0
0.1 g./d. temp., °C.	221	208	245
1.0 g./d. temp., °C.	220	207	243

^a At 1% strain.

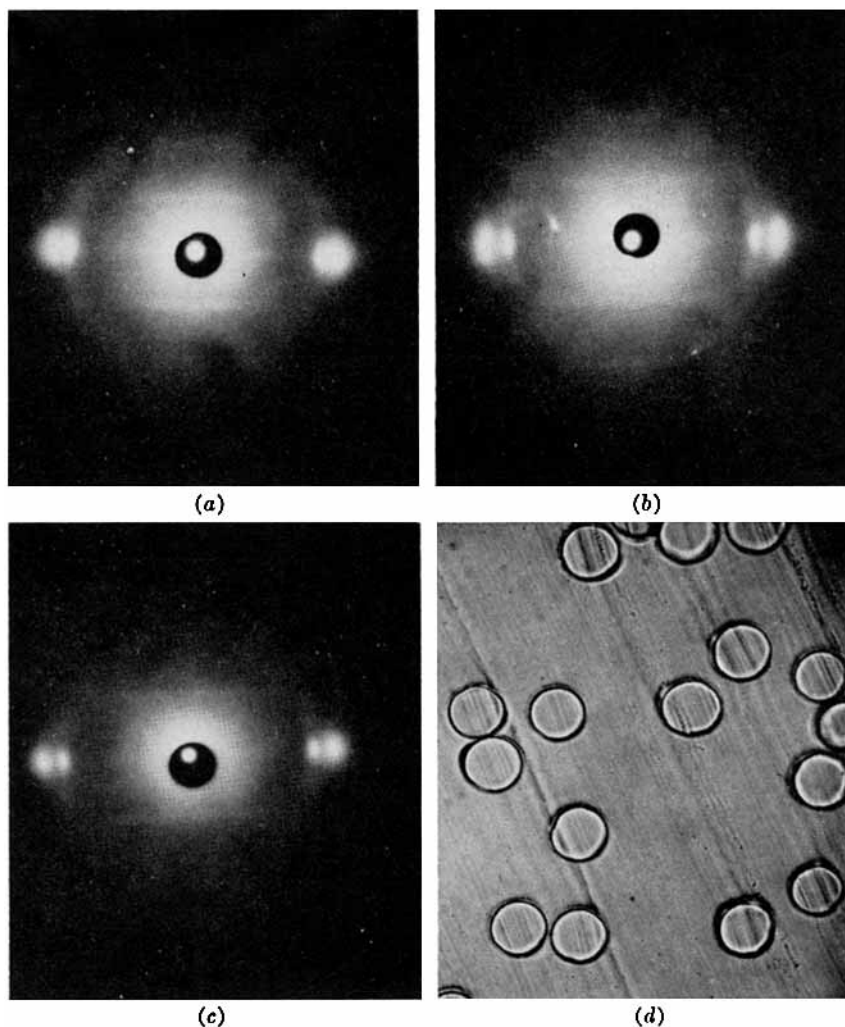


Fig. 1. X-ray diffraction pattern of (a) nylon 7; (b) nylon 6; (c) nylon 66; and (d) cross section of nylon 7 filament yarn.

antiparallel aligned molecules, which in turn varies with the number of C atoms in the amino acid and whether even or odd.¹²

Nylon 7 was melt spun at temperatures between 280 and 290°C. into yarns containing 30 filaments which were hot-stretched about 400% at commercial draw ratios and take-up rates. Because of the low content of extractables (1.5%), no extraction of the resin before spinning or of the fiber after spinning was necessary.

The textile properties of a nylon 7 yarn (250/30) are compared in Tables VIIIA and B with those of a commercial tire-cord of nylon 6 (840/140) and a high tenacity nylon 66 (210/34).

It is interesting to note in Table VIIIB that the tenacities of all three nylons drop off with increasing temperature at essentially the same rate up

to 180°C., where the tenacity of nylon 6 declines more rapidly. With increasing temperature the stiffness of nylon 6 declines more rapidly than the other two nylons which have roughly parallel stiffness-temperature curves below the melting region. The stiffness moduli are in the order of nylon 66 > nylon 7 > nylon 6 at all temperatures.

TABLE VIII B
Temperature-Tenacity-Stiffness Relationship

Temp., °C.	Tenacity, g./d.			Stiffness, g./d.		
	7	6	66	7	6	66
25	7.7	7.8	8.0	42	38	50
60	6.3	6.8	7.1	27	24	36
100	5.5	5.8	6.1	15	11	20
140	4.6	4.9	5.2	11	7.2	13
180	3.6	3.8	4.0	8.5	4.2	9.7
200	3.2	2.3	3.5	7.0	2.7	8.8
220	0.7	—	2.9	3.6	—	7.2

The x-ray diffraction patterns of the three high tenacity nylons are compared in Figure 1, which also shows the cross section of nylon 7 filament yarn. The x-ray patterns show a comparable degree of crystallinity for all three nylons. Although all three fibers are highly oriented, there is obviously a difference in degree. Nylon 6 appears to have less orientation relative to nylons 7 and 66; nylon 66 shows the highest degree of orientation.

Studies on the resiliency and abrasion resistance showed that these properties are essentially the same for all three nylons. The dyeability of nylon 7 is comparable to that of nylon 66.

The authors wish to thank Dr. G. M. Bryant and Messrs. J. B. Arthur, J. S. Roberts, and R. L. Stultz for their contributions to this work.

References

1. Manasse, A., *Chem. Ber.*, **35**, 1367 (1902).
2. Carothers, W. H., and G. J. Berchet, *J. Am. Chem. Soc.*, **52**, 5289 (1930).
3. Novotny, A., U. S. Pat. 2,579,851 (December 25, 1951).
4. Coffman, D. D., N. L. Cox, E. L. Martin, W. E. Mochel, and F. J. Van Natta, *J. Polymer Sci.*, **3**, 85 (1948).
5. Wiloth, F., *Kolloid-Z.*, **160**, 48 (1958).
6. Schaaf, S., *Faserforsch. u. Textiltech.*, **10**, 328 (1959).
7. Nesmejanow, A., et al., *Chem. Techn. Berlin*, **9**, 139 (1957); N. V. Mikhailov et al., *Vysokomolekulyarne Soedineniya*, **1**, 185 (1959).
8. Starcher, P. S., and B. Phillips, *J. Am. Chem. Soc.*, **80**, 4079 (1958).
9. Starcher, P. S., and B. Phillips, U. S. Pat. 2,839,776 (June 17, 1959).
10. Union Carbide Corp., French Pat. 1,210,137 (December 28, 1959).
11. Horn, C. F., British Pat. 857,062 (December 29, 1960); British Pat. 857,657 (December 29, 1960).
12. Hill, R., and E. Walker, *J. Polymer Sci.*, **3**, 609 (1948).

Synopsis

Eight esters of 7-aminoheptanoic acid were prepared as monomers for nylon 7 (polyheptanamide). They were made from ϵ -caprolactone via the route; 6-chlorohexanoic acid, alkyl-6-chlorohexanoate, alkyl-6-cyanohexanoate, alkyl-7-aminoheptanoate. The stability of these esters against polymer formation during distillation and at room temperature increased with the number of C atoms in the alcohol. When the esters were heated at 270°C. to form the polyamide, the same trend in stability was observed; the polyamides obtained were of too low molecular weight for melt spinning. Upon heating ethyl-7-aminoheptanoate with water (mole ratio 1 to >3) at 100°C., a mixture of 7-aminoheptanoic acid with mainly dimeric acid and ester was obtained. This product ("precursor") was a stable solid at room temperature which could readily be converted at atmospheric pressure within 2 hr. to high molecular weight, spinning grade nylon 7. The melting point, density, moisture regain, and sticking temperature of nylon 7 were compared with those of nylons 6, 8, 9, 10, and 11. Nylon 7 was melt spun into high tenacity yarn and its textile properties were discussed in comparison with those of nylons 6 and 66. The low oligomer content of nylon 7 (1.5%) made extraction of the resin before spinning unnecessary.

Résumé

On a préparé huit esters de l'acide-7-aminoheptanoïque devant servir de monomères pour le nylon-7 (polyheptanamide). On les a synthétisé, à partir de l' ϵ -caprolactone via l'acide-6-chlorohexanoïque, le 6-chlorohexanoate d'alcoyle, le 6-cyanohexanoate d'alcoyle pour arriver finalement au 7-aminoheptanoate d'alcoyle. La stabilité de ces esters vis-à-vis de la polymérisation pendant la distillation ou à température ambiante, augmente avec le nombre d'atomes de carbone dans l'alcool. Lorsqu'on chauffe les esters à 270°C pour former le polyamide, on observe la même échelle de stabilité; les polyamides obtenus étaient de trop bas poids moléculaire pour être filés à l'état fondu. Par chauffage du 7-aminoheptanoate d'éthyle en présence d'eau (rapport molaire 1 à >3) à 100°C, on obtient un mélange d'acide-7-aminoheptanoïque avec principalement un acide et un ester dimériques. Ce produit ("précurseur") était un solide stable à température de chambre qui peut être transformé facilement à pression atmosphérique, en 2 heures, en un nylon 7 filable de haut poids moléculaire. On a comparé le point de fusion, la densité, le regain d'humidité et la température de rétrécissement du nylon 7 aux propriétés correspondantes des nylons 6, 8, 9, 10, et 11. Le nylon 7 a été filé à l'état fondu en fils de ténacité élevée et ses propriétés textiles sont discutées en les comparant avec celles des nylon 6 et 66. Le faible contenu en oligomère du nylon 7 (1.5%) rend l'extraction de la résine nécessaire avant la filature.

Zusammenfassung

Acht Ester der 7-Aminoheptansäure wurden als Monomere für Nylon 7 (Polyheptanamid) hergestellt. Diese Verbindungen wurden aus ϵ -Caprolacton auf folgendem Wege hergestellt: 6-Chlorhexansäure, Alkyl-6-chlorhexanat, Alkyl-6-cyanhexanat, Alkyl-7-aminoheptanat. Die Stabilität dieser Ester gegen die Bildung von polymeren Produkten bei Zimmer-temperatur und während der Destillation wächst mit der Anzahl der Kohlenstoffatome in den alkoholischen Alkyl-Gruppen. Sehr ähnliche Stabilitätsverhältnisse wurden beim Erhitzen der Ester auf 270°C zur Bildung des hochmolekularen Polyheptanamids beobachtet. Die auf diese Art hergestellten Polyamide konnten wegen ihres zu niedrigen Molekulargewichts nicht schmelzversponnen werden. Wenn man Äthyl-7-aminoheptanat mit Wasser im Molverhältnis 1: >3 für einige Zeit auf 100°C erhitzt, so erhält man eine Mischung von 7-Aminoheptansäure, dimerer Säure und dimerem Ester. Dieses Produkt (als "precursor" bezeichnet) ist bei Zimmer-temperatur ein fester Stoff. Innerhalb von 2 Stunden kann der "precursor" durch Erhitzen bei Normaldruck in hochmolekulares, schmelzspinnbares Polyheptanamid

umgewandelt werden. Schmelzpunkt, Dichte, Feuchtigkeitsaufnahmevermögen und Erweichungstemperatur des Nylon 7 werden mit den entsprechenden Eigenschaften der Nylons 6, 8, 9, 10 und 11 verglichen. Nylon 7 wurde zu hochfesten Fäden schmelzversponnen. Der niedrige Oligomergehalt (1,5%) des Nylon 7 macht die Extraktion des Polymeren vor dem Schmelzspinnen überflüssig. Die textilen Eigenschaften des Nylon 7 werden im Vergleich mit Nylon 6 und Nylon 66 diskutiert.

Received December 22, 1961