9(10)-Carboxyoctadecylamine and 9(10)-Aminomethyloctadecanoic Acid: Synthesis and Polymerization to Polyamides with Lateral Substitution[1]

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ABSTRACT

9(10)-Carboxyoctadecylamine (I) and 9(10)-aminomethyloctadecanoic acid (II) have been prepared from selectively hydroformylated oleonitrile and oleic acid, respectively. Polymerization of I gave a transparent hard, somewhat brittle, polyamide, whereas polymerization of II gave a soft, rubbery polymer that flowed slowly at room temperature. Copolymers of I with II had properties reflecting those of the component homopolymers, although II exercised a disproportionate softening effect. The same was generally true of copolymers of I or II with nylon-66 salt, caprolactam, and 9-aminononanoic acid. The copolymer of I with 25 mole % nylon-66 salt was transparent, was also elastic, and could be either drawn into fibers or made into a coherent film. The properties of the two amino acids and of their polymers agreed with those expected from simpler alkyl-substituted amino acids.

INTRODUCTION

The preparation of transparent polyamides for packaging materials, films, coatings, and fibers is receiving increasing attention in the patent literature (1-8). Transparency can result from side chains that hinder crystallinity of the main polymer chain (9). Polyamides with elastomeric properties also could serve in the applications mentioned.

The C-19 alkyl-substituted ω-amino acids, 9(10)-carboxyoctadecylamine (I) and 9(10)-aminomethyloctadecanoic acid (II), were prepared from products of rhodium-triphenylphosphine catalyzed selective hydroformylation (10) as shown in Figure 1. Polymers of I and II are novel polyamides with lateral substitution. These polyamides are transparent, and they either are more or less elastomeric or can confer this property on copolymers with nylon-66 salt, caprolactam, and 9-aminononanoic acid.

EXPERIMENTAL PROCEDURES

Oleonitrile was prepared by the reaction of oleic acid (Pamolyn 100, Hercules, Inc., Wilmington, Del., 96% oleic acid) with urea (11 and R.E. Burks, Jr., private communication). 9(10)-Formylstearic acid was prepared by selective hydroformylation of oleic acid (10).

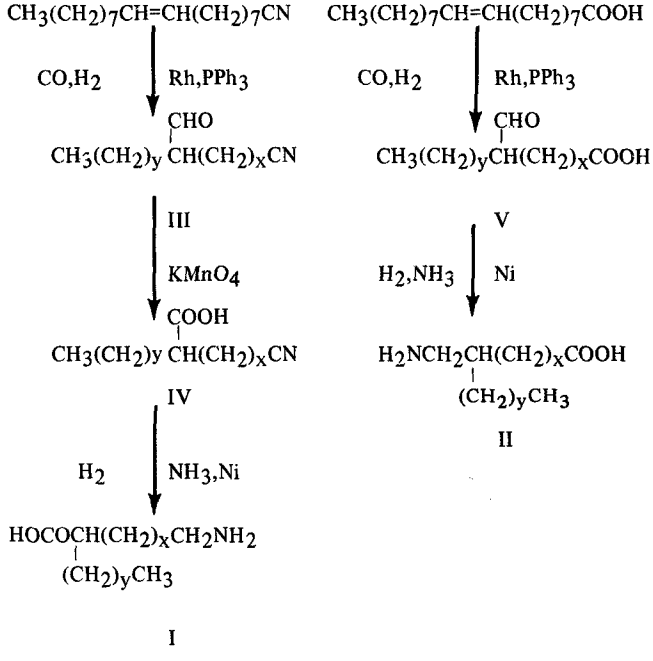

FIG. 1. The C-19 alkyl-substituted ω-amino acids, 9(10)-carboxyoctadecylamine (I) and 9(10)-aminomethyloctadecanoic acid (II), prepared from products of rhodium-triphenylphosphine catalyzed selective hydroformylation (10). x = 7, y = 8; x = 8, y = 7

Analytical Methods

The mp were determined with a DuPont 900 differential thermal analyzer equipped with a -100-500 C cell (liquid nitrogen coolant) with micro- and macroheat blocks under the following conditions: 2 scf/min nitrogen cell flow, 5 C/min heating rate; microsample tube loaded to 2 mm depth for crystalline samples or macrosample tube to 4 mm for liquids; SiC reference; T axis at 0.2 C/in.; T axis at 20 C/in. Polymer softening points were determined with a DuPont 940 thermomechanical analyzer equipped with a quartz penetration probe with 0.025 ± 0.001 in. diameter Invar tip under the following conditions: 5 g probe loading, 5 C/min heating rate; samples ca. 3 mm diameter, 1 mm deep. The probe was adjusted to touch the sample surface at the starting temperature. The sample was cooled in liquid nitrogen and heated in air. ΔT Axis 0.02 mV/in. or ca. 0.85 mil sample displacement/in. chart paper, T axis 20 C/in.

Gas liquid chromatographic (GLC) data were obtained with a Hewlett-Packard F&M model 810 temperature programed chromatograph equipped with hydrogen flame

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detectors and operated with a 290 C glass-lined injection port and 300 C detector temperatures. The detector was operated with 100 cc/min hydrogen and 600 cc/min air-flow rates. The chromatograph was operated in the single column mode with all columns being 122 cm x 2 mm inside diameter stainless steel. All runs were programed at 8 C/min from 150-300 C with 50 cc/min helium carrier gas flow. The electrometer was operated at 10^3 range and attenuation 1.

Because each product required a somewhat different GLC procedure, these procedures are given in some detail. Carboxystearonitrile (10-20 mg) was silylated (12) with 0.5 ml N,O-bis(trimethylsilyl)trifluoroacetamide (Regis Chemical Co., Chicago, Ill.) at room temperature for 5 min in a septum-covered vial previously purged with nitrogen. The reaction mixture was injected on a column loaded with 4.0% SE-30 on 80-100 mesh HP Chromosorb G (Applied Science, State College, Pa.). Absolute retention time, 11.34 min.

Aminomethyloctadecanoic acid (10-20 mg) was silylated with 0.5 ml N,O-bis(trimethylsilyl)trifluoroacetamide at 150-155 C for 15 min under nitrogen in a 19 x 65 mm vial equipped with a Teflon-lined cap. Only the sample portion of the vial was heated (oil bath) to permit the mixture to reflux. After cooling to room temperature, the solution (0.3 μliter) was injected on a column loaded with 5% OV-17 on 80-100 mesh AW HMDS Chromosorb W (Supelco, Bellefonte, Pa.). Retention time for the disilyl derivative was 14.09 min.

Into a 10-50 mg sample of carboxyoctadecylamine in a nitrogen-purged vial fitted with a silicone-rubber septum was injected 0.4 ml trifluoroacetic anhydride (Eastman White Label) followed immediately by 0.5 ml distilled 1-butanol, which had been stored over $CaSO_4$ (13,14). The vial was shaken, and the contents (0.1-0.2 μliter) were injected immediately on a column loaded with 5% OV-17 on 80-100 mesh AW HMDS Chromosorb W. The derivative appeared as one sharp peak. Absolute retention time was 12.95 min. Regardless of preparation conditions, the silyl derivative of carboxyoctadecylamine appeared as di- and mono- (free NH_2) silyl peaks. Summation of these peaks gave ca. the same quantitative results as those from the butanol-quenched trifluoroacetyl derivative.

GLC analyses do not indicate isomeric composition. No separation of isomers was observed. Because of isomeric heterogeneity, a product of high GLC purity may have a fairly wide melting range.

Mol wt were determined by vapor-pressure osometry of chloroform solutions.

9(10)-Formylstearonitrile (III)

A 1 liter rocker-shaker autoclave (Autoclave Engineers, Erie. Pa.) was charged with 380 g oleonitrile (95.8% by GLC, 1.38 moles), 7.6 g rhodium-on-carbon (5%) (Engelhard, Murray Hill, N.J.), 3.8 g triphenylphosphine (Strem, Danvers, Mass.), and 100 ml toluene. Hydroformylation was carried out at 110 C and 2000 psig synthesis gas (H_2:CO, 1:1) until gas absorption ceased (1.5 hr). The reactor was cooled to room temperature and vented; the contents were filtered through a medium porosity fritted glass funnel. After the reaction mixture was stripped on a rotary evaporator, a crude dark-brown product resulted (429 g, 94.6% III by GLC), which was used directly for the next reaction.

9(10)-Carboxystearonitrile (IV)

9(10)-Formylstearonitrile (III, 210 g, 94.6% purity, 0.67 mole) was dissolved in 1500 ml acetone and 100 ml water in a 4 liter Erlenmeyer flask. The flask was placed in an ice bath, and the solution was stirred vigorously. Solid potassium permanganate (78 g, 0.49 mole) was added over 35 min. During this time, the temperature rose from 0-16 C. Stirring was continued for a total of 2.5 hr. Water (500 ml) was added, and the mixture was acidified with concentrated hydrochloric acid (45 ml). Sodium metabisulfite was added to dissolve MnO_2, with sufficient additional hydrochloric acid to maintain an acidic medium. Excess acid then was neutralized by addition of solid sodium bicarbonate. The organic layer was separated, filtered, and stripped at <40 C to leave a yellow emulsion that was transferred to a separatory funnel. Ca. 100 ml water was separated, and 400 ml ether was added. The emulsion was broken by addition of 100 ml saturated salt solution. The ether layer was separated, filtered, and dried over sodium sulfate. The dried ether solution was stripped to leave 212 g bright yellow liquid, n_D^{20} 1.4600, mp -36.4 to -31.8 C, 97.2% IV by GLC (99% yield).

This product (79 g, 0.25 mole) was dissolved in a solution of 10 g (0.25 mole) sodium hydroxide in 300 ml water. The solution was stirred magnetically in an ice bath, and 22 ml 5 N hydrochloric acid (0.11 mole) was added. After ca. 10 min, a solid began to form. Stirring was continued for ca. 1 hr, and the mixture was left in the ice bath for an additional 2.5 hr. The solid then was filtered, washed with cold water, air-dried, and finally dried in the vacuum oven at 40 C to give 68 g (95%) acid salt. The filtrate was acidified and extracted with ether to recover 10 g bright yellow liquid. The dried acid salt was stirred vigorously with 300 ml ether for 0.5 hr, filtered, and air-dried to give 64 g acid salt, mp 81.1-85.0 C.

Analysis calculated for $C_{38}H_{69}N_2NaO_4$: carbon, 71.21; hydrogen, 10.85; nitrogen, 4.37; sodium, 3.59. Found: carbon, 70.81; hydrogen 11.16; nitrogen, 4.24; sodium, 3.34.

Evaporation of the ether wash gave 3 g yellow liquid, which solidified on standing.

The acid salt (63 g) was placed in a separatory funnel with 100 ml ether, 50 ml water, and 50 ml 5 N hydrochloric acid. This mixture was shaken vigorously, the ether layer separated, and the aqueous layer was extracted with another 100 ml ether. The combined ether extracts were washed with 100 ml 2.5 N hydrochloric acid and two 100 ml portions of water, filtered and dried over magnesium sulfate. After drying, the solution was stripped to leave 59 g (97%) 9(10)-carboxystearonitrile (IV), mp -33.8 to -29.8 C, n_D^{20}1.4593, 99.7% pure by GLC.

Analysis calculated for $C_{19}H_{35}NO_2$: carbon, 73.74; hydrogen, 11.40; nitrogen, 4.52. Found: carbon, 73.75; hydrogen, 11.63; nitrogen, 4.39.

Distillation of IV resulted in some decomposition and a product of lower purity.

9(10)-Carboxyoctadecylamine (I)

A 1000 ml Magne-Dash autoclave was charged with 53 g (0.17 mole) IV, 180 ml (ca. 120 g, 7 moles) liquid ammonia, 320 ml methanol, and 5 g no. 28 Raney nickel catalyst (W.R. Grace, South Pittsburg, Tenn.) that had been washed repeatedly with methanol. The reduction was carried out at 2000 psig hydrogen pressure and 125 C for 4 hr. After the reactor was cooled and vented, the catalyst was removed by filtration through a mat of filter-aid. The filtrate was stripped on a rotary evaporator to leave 59 g green solid, 99.8% I by GLC. Product I was dissolved in 700 ml boiling methanol, and the solution was filtered to remove a small quantity of insoluble material. Portions of the clear green filtrate were mixed with measured quantities of a methanol solution of dimethylglyoxime (10 mg/ml) to determine the amount required to remove the nickel. A total of 150 ml solution (1.5 g dimethylglyoxime, equivalent to ca. 0.4 g nickel) was added to the entire filtrate. The red precipitate was removed by filtration, and the bright yellow filtrate was concentrated to ca. 500 ml. This solution was stirred, while cooling in an ice bath. Ca. 250 ml ether was added and stirring continued for 1 hr. The mixture was filtered,

and the filter cake was washed with methanol. After the filtrate was concentrated to ca. 200 ml and cooled in the ice bath as before, 200 ml ether was added. After 2.5 hr, the mixture was filtered; the filter cake was washed with methanol and then combined with the first crop. After air-drying at room temperature, the light pink product weighed 45 g (85% yield based upon IV), mp 149-158 C, 99.8% pure by GLC. The filtrate was stripped to leave 2.8 g residue.

At room temperature, 35 g pink product was stirred with 150 ml methanol for 3 hr. The slurry was filtered, and the filter cake was reslurried 4 hr. The twice slurried filter cake then was mixed with 200 ml methanol, and the mixture was heated to boiling on a steam cone. The hot solution was stirred, while cooling to room temperature and then filtered. The filter cake was washed with methanol. The filtrate contained additional solid so it was reheated, cooled, and refiltered to give a second crop of solid. The filtrate then was concentrated to ca. 150 ml and stored in a refrigerator overnight. Filtration gave a third crop of product. The combined crops were air-dried to give 24.4 g (69% recovery) white 9(10)-carboxyoctadecylamine (I), mp 153-159 C, 100% pure by GLC.

Additional I of good purity and color could be recovered by repeated slurrying and recrystallizing. A somewhat more crystalline I, with a slightly sharper mp, was obtained as follows: 10 g purified I was mixed with 100 ml methanol, and the mixture was heated to boiling on the steam cone. The hot mixture was filtered; 2.1 g did not dissolve. The clear filtrate was stirred in an ice bath, and 5 ml water was added. After 1 hr, the crystallized I was filtered, washed with methanol, and air-dried to give 7.2 g (91% of dissolved I) granular product, mp 155-158 C, 100% pure by GLC. The IR spectrum was consistent with structure I with bands at 2551, 1613, 1508, and 1117 cm^{-1} (NH_3^+) and at 1449 cm^{-1} (COO^-), as well as the normal bands associated with hydrocarbon chains. The NMR spectrum is reported together with that of II below.

Analysis calculated for $C_{19}H_{39}NO_2$: carbon, 72.79; hydrogen, 12.54; and nitrogen, 4.47. Found: carbon, 72.51; hydrogen, 12.60; and nitrogen, 4.37.

9(10)-Aminomethyloctadecanoic Acid (II)

A 1000 ml Magne-Dash autoclave was charged with 71 g 9(10)-formylstearic acid (V) (89% pure, 0.2 mole), 100 ml aqueous ammonia (29% ammonia, 1.5 moles), 16 g no. 28 Raney nickel catalyst that had been washed repeatedly with methanol, and 400 ml methanol. The reaction was carried out at 1000 psig hydrogen pressure and 100 C for 2 hr. After the reactor was cooled and vented, the catalyst was removed by filtration through a mat of filter-aid, and the filtrate was concentrated to ca. 200 ml on a rotary evaporator. Ca. 300 ml ether was added, and the mixture was stored at -20 C for 2 days. The crystallized solid was filtered, washed with cold ether, and air-dried to give 35 g light green solid, 96% II by GLC (53% yield), mp 95-111 C. The filtrate was stripped to leave 36 g viscous green liquid from which a small amount of additional solid could be obtained by repeated crystallization from methanol-ether. The residual viscous liquid analyzed 60% II by GLC.

Nickel was removed from the crude product with dimethylglyoxime, as described for I. After filtration of the precipitate, 100 ml resulting methanol solution, containing ca. 20 g product, was stirred with 100 ml ether in an ice bath. Water (ca. 50 ml) was added to initiate crystallization. After stirring for 1 hr, the mixture was filtered, and the solid amino acid II was washed with ether and air-dried. Recovery was 11.4 g, 98.6% pure by GLC, mp 115-121 C. This product (10 g) was dissolved in 50 ml boiling ethanol. The hot solution was filtered, and the volume of the filtrate was brought to 75 ml. The solution was stirred in an ice bath for 20 min to initiate crystallization and then stored in the refrigerator overnight. The cold mixture was filtered, the filter cake was washed with cold ethanol, and air-dried to give 7.4 g 9(10)-aminomethyloctadecanoic acid, 99.3% pure II by GLC, mp 119-123 C. The IR spectrum showed bands at 2632, 1515, and 1419 cm^{-1} (NH_3^+) and at 1587 and 1460 cm^{-1} (COO^-), together with normal long chain hydrocarbon bands. NMR spectra of I and II were measured at 100 MHz on a Varian HA-100 spectrometer with tetramethylsilane ($\delta=0$) as internal standard. The solvent was methanol-d_4. The spectra have several similar features: a terminal methyl group appears at δ0.9, the large methylene peak at δ1.3, and the methylene α to the carbonyl at δ2.2. The distinguishing feature in the NMR spectra of the two compounds is the appearance of the methylene bearing the amino group. In II, the methylene group resonates at δ2.80 and is a doublet (J=7Hz). The appearance of a doublet indicates there is only one proton on the carbon adjacent to the amino carbon. The spectrum of I contains a triplet absorption at δ2.86 (J=7Hz) assigned to the amino methylene protons. The triplet pattern indicates two protons are on the carbon adjacent to the amino carbon.

Analysis calculated for $C_{19}H_{39}NO_2$: carbon, 72.79; hydrogen 12.54; and nitrogen, 4.47. Found: carbon, 72.27, hydrogen, 12.36; and nitrogen, 4.35.

Some additional impure II could be recovered from the mother liquors.

Polymerization

Polymerizations (14,15) were carried out with 2-5 g samples in 10 or 25 ml distilling flasks. The flask was fitted with a nitrogen inlet capillary and a second flask as receiver for evolved water. The receiver outlet was attached to a bubble counter. Before heating, the system and sample were purged with nitrogen which had been passed through a coil of Oxy-Sorb (Alltech Associates, Arlington Heights, Ill.), and nitrogen flow was continued during polymerization. The polymerization flask was immersed in a Wood's metal bath, preheated to the desired temperature, for the required time. Conditions for polymerizations and properties of the polymers are given in Tables I and II. Ca. 5 min before heating was stopped, the nitrogen capillary was pulled from the molten polymer. The flask then was removed from the bath, cooled, and broken to recover the polymer. Most samples of polymerized II adhered strongly to the glass. Various mold-release agents were ineffective in overcoming this adherence. Polymerized I generally separated from the glass easily.

RESULTS

In contrast to conventional procedures which give a complex mixture of isomers, selective hydroformylation of oleic acid with rhodium-triphenylphosphine catalyst yields 9(10)-formylstearic acid (V) (10). The same selectivity occurs when other monounsaturated substrates, like oleonitrile, are used. Availability of these compounds suggested their use in the preparation of monomers, such as amino acids for polyamides. Two amino acids could be prepared quite readily. Reduction of IV (from oxidation of hydroformylated oleonitrile) to I was carried out with Raney nickel catalyst in ammoniacal methanol. Evaporation of the filtered reaction solution gave a solid product in excellent yield and purity.

Preparation of primary amines by reductive alkylation of ammonia with aldehydes is well known (16). The reaction was successful with V to yield II directly. Unlike I, II could not be isolated satisfactorily from the reaction solution by simple evaporation. When evaporation was tried, quantities of viscous material accompanied the product. GLC indicated that this material contained significant quantities of II which could not be isolated. Solid II was obtained from the reaction solution by concentration and addition of

TABLE I

Polymerization of 9(10)-Carboxyoctadecylamine (I) and 9(10)-Aminomethyloctadecanoic Acid (II)

Monomer	Polymerization temperature, C	Time, hr	$\bar{M}$	T_s, C[a]
I	260-264	2	5343	24
	260-268	6	5677	21
	260-265	8	6264	24
	197-203	30	5798	31
II	265-270	2	2271	- 9
	260-266	6	2500	-11
	261-270	8	2271	- 9
	197-203	30	3244	-10

[a]Extrapolated softening temperature by thermomechanical analysis (see text).

ether followed by crystallization from this mixed solvent. Neither yield nor purity was as high as with I.

Both I and II as isolated from their reaction solutions contained nickel, as shown by their green color. This contaminant was removed by treating solutions of the amino acids with dimethylglyoxime and filtering the precipitated red nickel-dimethylglyoxime complex. A fairly delicate balance was required to make sure that all the nickel was removed without leaving an excess of dimethylglyoxime. The last traces of nickel complex were removed by repeated slurrying of the product with ethanol. Additional purification was obtained by crystallization of I from methanol-ether and of II from ethanol. A more crystalline form of I was obtained from methanol-water.

Polymerizations of both I and II proceeded readily at atmospheric pressure (14,15,17). Some preliminary experiments were run to determine the effect of small variations in monomer purity, as determined by GLC, but no significant differences in polymerization or polymer properties were observed. Striking differences were found between polymers of the two amino acids. Polymerization of I gave a clear, hard, rather brittle polymer. The polymer from II under the same conditions was soft and rubbery and flowed slowly at room temperature.

Table I gives conditions for homopolymerization of I and II and properties of the polymers. Polymers were characterized by mol wt, determined by vapor pressure osmometry in chloroform, and by softening temperature, determined by thermomechanical analysis (TMA).

TMA records the temperature at which a probe, under specified loading, penetrates the polymer surface. The softening temperatures, T_s in Tables I and II, are extrapolated from TMA curves. For almost all the polyamides, this temperature is considerably lower than the temperature at which the polymer apparently melts. Probably T_s is more a measure of glass transition temperature (T_g) than a melting temperature (T_m) (18 and E.R. Rogier, private communication). Polymerized I, which was hard and brittle, typically has a softening temperature of ca. 21 C. The typical softening temperature of polymerized II is -11 C. Softening temperatures of copolymers with nylon-66 increase with increased proportions of nylon-66. When this proportion is 76 mole % with either I or II, T_s >200 C lies beyond the range of the instrument. Copolymers with caprolactam show a similar overall relationship, although there are apparent discontinuities.

Polymerized samples of I generally could be separated easily from the glass when the flask was broken after polymerization. With polymerized II, however, removal from the glass was all but impossible. Polymerized I usually could be cut with a knife and hammer, while polymerized II could be cut much more easily. Both polymers were readily soluble in chloroform.

Under analogous conditions (Table I), I polymerized to a higher mol wt than II did. Increased polymerization time at 260 C increased mol wt with I but affected II little, if at all. Extended polymerization (30 hr) at a lower temperature (200 C) increased the mol wt with II but not with I. In the range of mol wt obtained, the softening temperatures were essentially constant.

Standard conditions for copolymerization were chosen at 260 C and 6 hr. Exact replication of conditions was not possible. A reasonable uniformity was achieved, except in a few instances where the heat needed to maintain the temperature was greater than expected.

TABLE II

Copolymers of 9(10)-Carboxyoctadecylamine (I) and 9(10)-Aminomethyloctadecanoic Acid (II)

Monomer	Mole %	Monomer[a]	Mole %	Polymerization temperature, C[b]	$\bar{M}$	T_s, C[c]	Transparency[d]
I	75	II	25	259-268	4504	7	T
I	50	II	50	259-268	4395	- 1	T
I	25	II	75	259-268	2930	- 1	T
I	90	66	10	255-257	4698	12	T
I	75	66	25	255-257	3244	21	T
I	50	66	50	253-267	e	(18) 159	C
I	24	66	76	254-261	e	>200	O
II	75	66	25	252-256	2725	-16	T
II	50	66	50	253-267	e	-2, 136	C
II	24	66	76	254-261	e	>200	O
I	80	6	20	257-263	4129	15	T
I	50	6	50	259-267	1627	2	C
I	25	6	75	258-260	e	19	C
I	10	6	90	262-269	e	179	O
II	80	6	20	257-263	2137	- -6	T
II	59	6	41	262-269	1730	-11	T
II	50	6	50	259-267	1652	-5 (22)	T
II	25	6	75	258-260	e	-6, 81	C
II	10	6	90	262-265	e	181	O
II	69	9	31	225-237	3097	-2	C
II	12	9	88	224-234	e	186	O

[a]66 = Nylon-66 salt, 6 = caprolactam, 9 = aminononanoic acid.

[b]Polmerization time 6 hr except with 9, 4 hr.

[c]Extrapolated softening temperature by thermomechanical analysis. See text. Temperatures in parentheses are secondary inflection points.

[d]T = transparent, C = cloudy, and O = opalescent.

[e]Insoluble in chloroform.

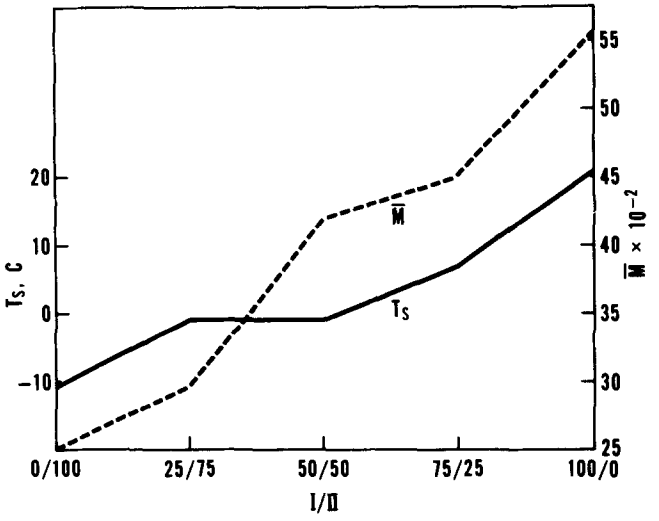

FIG. 2. Mol wt ($\bar{M}$) and softening points (T_s) of copolymers of 9(10)-carboxyoctadecylamine (I) with 9(10)-aminomethyloctadecanoic acid (II).

Conditions for copolymerization of I with II are given in Table II; properties of the copolymers (Table II and Fig. 2) essentially reflect those of the homopolymerized components. The effect of II in lowering softening temperature was disproportionate.

Copolymerization of either I or II with caprolactam went smoothly under standard conditions. Water generated by polymerization of the amino acid initiated copolymerization of the lactam. Mol wts were lower than for homopolymers, especially at the 50 mole % level, with correspondingly lower softening temperatures; however, the lowest mol wt does not correspond with the lowest softening temperature. With more than 50 mole % caprolactam, the polymers became less transparent and were insoluble in chloroform, so that mol wt were not determined.

Nylon-66 salt, an equimolar mixture of hexamethylenediamine and adipic acid, also copolymerized readily with I or II. Results (Table II) were similar to those with caprolactam, although mol wts were higher, softening temperatures generally were higher, and chloroform solubility was lower.

Several copolymers showed two TMA inflection points. For 50:50 mixtures of II/66 and 25:75 mixtures of II/caprolactam, both inflections were of ca. equal magnitude. Presumably the first inflections represented transition temperatures and the second, actual softening points.

The copolymer of I with 25 mole % nylon-66 salt was elastic. Fibers could be drawn from this polymer and a coherent film made. Both fiber and film regained their original dimensions after stretching. The copolymer of I with 10 mole % nylon-66 had similar properties but was harder and more brittle.

Two copolymers of II with 9-aminononanoic acid were prepared (Table II). Nylon-9 prepared under similar conditions had a mol wt of ca. 20,000 (14).

DISCUSSION

The two amino acids I and II are structural isomers. Each structural isomer is an equimolar mixture of positional isomers with the substituent in the 9 and 10 positions. Each positional isomer is made up of optical isomers. The structural isomerism affects properties of both monomers and polymers significantly. The effects of positional and optical isomerism are believed to be less important.

Both I and II are alkyl-substituted ω-amino acids. The substituent in I is α to the carboxyl group (in the 2 position). The aminomethyl group in II results in an alkyl substituent β to the amine function [the (x+2)-position]. Amino acids with these structures are not numerous. The known examples in Table III show that aminomethyl acids have significantly lower mp than corresponding 2-substituted acids. In the series of methyl-substituted 6-aminohexanoic acids, the 2-methyl acid has the highest mp and the 5-methyl acid (5-aminomethylhexanoic acid) the lowest. These relationships are altered when optically active substituted amino acids are considered (29), and they do not apply to the corresponding lactams (22).

TABLE III

Mp ω-Amino Acids

Structure	Mp, C	Reference
$H_2N(CH_2)_3CO_2H$	195	19
$H_2N(CH_2)_2\underset{\underset{CH_3}{\vert}}{C}HCO_2H$	210-215	20
$H_2NCH_2\underset{\underset{CH_3}{\vert}}{C}HCH_2CO_2H$	174	21
$H_2NCH_2\underset{\underset{C_2H_5}{\vert}}{C}HCH_2CO_2H$	178-180	20
$H_2N(CH_2)_4CO_2H$	158-161	19
$H_2N(CH_2)_5CO_2H$	210-212	19
$H_2N(CH_2)_4\underset{\underset{CH_3}{\vert}}{C}HCO_2H$	228-230	22
$H_2N(CH_2)_4\underset{\underset{C_2H_5}{\vert}}{C}HCO_2H$	186-187	23
$H_2N(CH_2)_4\underset{\underset{C_3H_7}{\vert}}{C}HCO_2H$	198.5-199	23
$H_2N(CH_2)_3\underset{\underset{CH_3}{\vert}}{C}HCH_2CO_2H$	187-188	24-26
$H_2N(CH_2)_2\underset{\underset{CH_3}{\vert}}{C}H(CH_2)_2CO_2H$	170-172.5	27
$H_2NCH_2\underset{\underset{CH_3}{\vert}}{C}H(CH_2)_3CO_2H$	145-147	24-26
$H_2N\underset{\underset{CH_3}{\vert}}{C}H(CH_2)_4CO_2H$	210-211	22
$H_2N(CH_2)_6CO_2H$	195	28

In these examples, the chain lengths of the acids and of the substituents are considerably shorter than those in I and II. Nevertheless, the mp relationship is borne out, since I melts ca. 35 C higher than II. The higher melting I was also easier to isolate and crystallize than II. Neither I nor II was appreciably soluble in water, but both were soluble in alcohols. These characteristics contrast to those of unsubstituted 9-aminononanoic acid, mp 195 C (14).

Although no attempt was made to isolate positional isomers, differential thermal analyses of I and II showed at least one significant endotherm before melting. No visual changes (in polarized or unpolarized light) were apparent at these temperatures. This behavior could result from some interaction between isomers, and the position and magnitude of the endotherm could reflect the isomer ratios. Overberger and Parker (30) have considered differences in crystal structure of enantiomers of C-methyl amino acids.

The properties of polymers of methyl-substituted ϵ-caprolactams (lactams of x-methyl-6-aminohexanoic acids) have been reported (31) (Table IV). On the basis of extractable material (monomer, low mol wt oligomers) and viscosity, the 5-methyl isomer had lower polymerizability and the polymer had a much lower mp than did the 2-methyl isomer. Polymers of the other isomers also melted higher than that of the 5-isomer. Again, optical activity in monomer and polymer alters these relationships (30,32). Polyamides from optically active caprolactams melt much

TABLE IV

Polymers of Methyl-Substituted ϵ-Caprolactam (31)

Polymer[a]	Extractable material, %	$\eta_{rel.}$[b]	Mp, C
$+NH(CH_2)_5CO+_n$	12	2.90	220
$+NH(CH_2)_4\underset{CH_3}{\underset{\vert}{C}}HCO+_n$	13	2.25	190
$+NHCH_2\underset{CH_3}{\underset{\vert}{C}}H(CH_2)_3CO+_n$	28	1.90	138

[a]Caprolactam polymerized 7 hr at 240 C; others, 14 hr at 250 C.
[b]Relative viscosity, 1 g polymer in 100 cc 94% sulfuric acid.

higher than those from racemates (32). Sweeny and Zimmerman (33) discussed the effect of lateral substitution upon polyamides.

The softening temperatures and mol wts of polymerized I and II agree with the published generalizations. Under analogous conditions, I polymerized to a higher mol wt than II. The softening temperature of polymerized I is higher than that of polymerized II. Overberger and Takekoshi (32) noted that, "Since CH_2NH and CH_2CO bonds have the highest freedom of rotation through the main chain, the substitution of a methyl group closest to the amide linkage may be the most effective way to impose rigidity on the polymer chain." Accordingly, polymerized I would be more rigid than polymerized II.

The mixtures of positional isomers will result in polymers of irregular spacing between amide groups in a single chain. Hence, there will be less hydrogen bonding between chains and lesser degrees of crystallinity. The presence of long alkyl groups as lateral substituents will cause an even greater reduction in hydrogen bonding with the result that polymers from I and II are transparent, low melting and soluble.

These factors are usually and properly cited in discussions of differences in mp of different polyamides (33). However, Rubin (34) observed that, for several series of nylons, the differences in mp between the nylon salts and their polymers vary only through a limited range. He suggested that where this approach is applicable, the difference in polymer mp is a consequence of the difference in mp of the starting materials. Amino acids I and II are inner salts, analogous to the diamine-diacid salts considered by Rubin, and they follow his observations. The difference between the mp of I and the softening point of its polymer is 158 - 21 = 137, whereas the corresponding difference for II and its polymer is 123 - (-11) = 134.

The polymers and copolymers of 9(10)-carboxyoctadecylamine and 9(10)-aminomethylstearic acid present many areas of theoretical and practical interest. As indicated at the beginning, transparent elastomeric polyamides, such as obtained from carboxyoctadecylamine and nylon-66, should find an increasing number of applications. Although we have terminated our work in this field, possibly others may want to continue.

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