R. S. MUROMOVA et al.

is less than the saturation concentration in the aqueous phase, polymerization occurs mainly on the particle surface, but if there is a monomer emulsion and its saturated solution in the aqueous phase, polymerization appears to occur inside them.

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SYNTHESIS AND POLYCONDENSATION OF cis- AND trans-ISOMERS OF y-(3-AMINOCYCLOHEXYL) BUTYRIC ACID *†

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OUR previous reports [1] dealt with the synthesis of *cis*- and *trans*-isomers of β -(3-aminocyclohexyl)propionic acid (*cis*- and *trans*-3-ACP) and polyamides on their base. Comparison between the properties of polyamide prepared by the polycondensation of *cis*-3-ACP and that previously prepared based of *cis*- β -(4-aminocyclohexyl)propionic acid [2] (*cis*-4-ACP) showed that the first had considerably higher melting point and a higher state of crystallinity than the second. The literature contains no other information on the properties of polyamides based on *cis*-isomers of 3- and 4- ω -amino acids of the cyclohexane series, nor of any other polymers as the products of the polycondensation of *cis*isomers of bifunctional derivatives of cyclohexane containing functional groups

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† IVth report of the series "Polyamides based on the amino acids of the cyclohexane series".

1504

in the 1,3- and 1,4-positions. We decided to find out whether the difference we had observed in the properties of polyamides on *cis*-3-ACP and *cis*-4-ACP base was only typical of this pair, or whether it could be taken as a general rule for all the polyamides of ω -amino acids of the cyclohexane series. We therefore synthesized *cis*- and *trans*-isomers of γ -(3-aminocyclohexyl)butyric acid (*cis*- and *trans*-3-ACB) and studied the products of their polycondensation.

Like the polyamides on their base, the individual *cis*- and *trans*-isomers of 3-ACB have not hitherto been described. There is a patent [3] on the preparation of a polyamide by polycondensation of a mixture of unknown composition of *cis*- and *trans*-isomers of this amino acid; the patent does not give the temperature range of the softening of this polyamide.

The synthesis of the *cis*- and *trans*-isomers of 3-ACB was performed on the following scheme [4, 5]:



On hydration of III, over a rhodium-platinum catalyst [6] in glacial acetic acid at 60° and 3 atm. a yield of 75% was separated of a product with m.p. 117-122° which, when recrystallized, produced a crystalline material with m.p. 127-128° (IV). The properties and elementary composition of this material correspond to γ -(3-N-acetylaminocyclohexyl)butyric acid. After hydration, the rest of the reaction mass (approx. 25%) is an oily material which does not crystallize if left for a long time. After hydrolysis of IV with dilute sulphuric acid and anionite purification, 3-ACB was obtained with m.p. 239-249° (VI). Hydrolysis of the oily product V produced free ACB with m.p. 228-229° (VII). On the basis of the current formulation of the Auvers-Skitt law for 1,3-disubstituted cyclohexane [7], and also on the basis of the fact that γ -(-3-N-acetylaminocyclohexyl)butyric acid with m.p. 127-128° (IV) is the principal reaction product of hydration in acid medium over an effective catalyst, VI can be ascribed *cis*-configuration and VII, *trans*-.

Original monomer	Polycondensation conditions	η*	m.p., °C†	Appearance of polymer
cis-3-ACB	1 hr 15 min—slow rise			
	at 270°	0.73	300-305	White caking powder
ditto	2 hr at 280°	0.54	300305	Transparent strong block
trans-3-ACB	4 hr at 250°	0.43	155 - 160	ditto
ditto	4 hr at 256°	0.52	155-160	ditto

POLYCONDENSATION OF cis- AND trans-y-(3-AMINOCYCLOHEXYL) BUTYRIC ACID

* B-specific viscosity of 0.5% solution of polymer in *m*-cresol at 20° .

† m.p. determined from thermomechanical curves.

The Table sets out the results of the polycondensation of the *cis*- and *trans*-3-ACB. On polycondensation both the 3-ACB isomers are completely converted into the corresponding polyamides, no bicyclic lactam formation being observed.

The polyamides of *cis*- and *trans*- 3-ACB are much more resistant to solvent than ordinary polyamides not containing aromatic or cyclohexane rings, or polyamides on *cis*-3-ACB base [1]. The polyamides of *cis*- and *trans*-3-ACB dissolve in phenol, cresol, concentrated sulphuric and trifluoroacetic acids; the *trans*-3-ACB polyamide, but not the one on *cis*-isomer base, is also soluble in concentrated formic acid and swells in concentrated hydrochloric acid. Neither of the polyamides dissolves when heated in 50% sulphuric acids, dimethylsulphone, α -piperidone or dimethylformamide. But the *cis*-3-ACP polyamide does dissolve in concentrated formic and sulphuric acid.



FIG. 1. Thermomechanical curves of the polyamides of cis-(1) and trans-y-(3-aminocyclohexyl)butyric acids (2).

Figure 1 shows the thermomechanical curves of the *cis*- and *trans*-3-ACB polyamides. The one on the *cis*-isomer base has a melting point 155° higher than that of the *trans*-isomer. Approximately the same difference in melting points was also found for polyamides in *cis*- and *trans*-3-ACP base [1].

Using the model spinning apparatus of [8], from the polyamide on cis-3-ACB base we produced strong elastic fibres of the higher number group, capable of orientation by stretching 4.0-4.5 times (forming temperatures 315-328°,

stretching temperature $150-190^{\circ}$ [9]. We compared the properties of the *cis*-3-ACB and *cis*-y-(4-aminocyclohexyl)butyric acid polymers (*cis*-4-ACB produced by Bogdanov, Kudryavtseva *et al.*) [10]. According to these authors, the *cis*-4-ACB polyamide has m.p. $195-210^{\circ}$, which is 100° lower than that of *cis*-3-ACB; besides this, in contrast to the *cis*-3-ACB polyamide, it does not form fibres from the melt. As with the polyamides of the *cis*-isomers of 3- and 4-ACP [1], this difference in the properties of polyamides based on the 3- and 4-ACB isomers must be due to a difference in the molecular conformation of the original amino acids. The equatorial position of the amino- and alkylene carboxyl group in the *cis*-isomer of ω -(-aminocyclohexyl)alkane acids gives high molecular symmetry and better macromolecular chain packing for the polyamide than does the axial equatorial position of these groups in the molecules of the *cis*-isomers of ω -(4-aminocyclohexyl)alkane acids.



FIG. 2. X-ray diffraction pattern of the polyamide of cis-(3-aminocyclohexyl)butyric acid.

The diffraction pattern shown in Fig. 2 is of cis-3-ACB, and it shows that this polyamide is highly crystalline. It was not possible to compare the crystallinity of polyamides of cis-3- and 4-ACB, as the work cited above [10] did not give any information on the crystallinity of the polyamide products. But since cis-4-ACB is unable to form fibres [10], this can be taken as indirect indication of its low crystallinity.

EXPERIMENTAL

 β -benzoyl propionic (I) [11] and β -(3-nitrobenzoyl)propionic (II) [12] acids were prepared in the usual way.

 γ -(3-N-acetylaminophenyl)butyric acid (III). 10 g II with m.p. 162–163° (according to [12] m.p. 165–166°) is suspended in a mixture of 15 ml glacial acetic acid and 15 ml acetic

R. S. MUROMOVA et al.

anhydride; 2 g palladium black is added and hydrated at 50° 3 atm. On completion of hydrogen absorption (approx. 4 hr) the catalyst is filtered off, and the acetic anhydride and acetic acid boiled away. The oily residue is heated with 20 ml water; on cooling 8.25 g III is separated, with m.p. 122–124°. A mixed sample, 1:1 with III prepared from II according to [4] and having m.p. 125–126°, melts at 122–124°.

cis- γ -(3-N-acetylaminocyclohexyl)butyric acid (IV). 10 g III, 45 ml acetic acid (purified by boiling in chromic anhydride), 1 g rhodium-platinum catalyst [6] is shaken up at 60° and 3 atm. until hydrogen absorption ceases, approx. 2.5 hr. The catalyst is filtered off, the acetic acid distilled off *in vacuo* under nitrogen. The residue is an oily material, which is mixed with 50 ml water. On cooling 7.27 g IV is separated with m.p. 117-122°. Yield 74% theoretical. After crystallizing twice from an alcohol-water mix (1:4) 5.19 g IV is obtained with m.p. 127.0-128.0°.

Found, %: C 63·48; 63·42; H 9·20; 9·37; N 6·35; 6·60. C₁₂H₂₁O₂N. Calculated, %: C 63·44; H 9·25; N 6·16.

cis-y-(3-aminocyclohexyl)butyric acid (VI). A solution of 1.75 g IV in 12 ml 20% sulphuric acid is heated for 72 hr with a reflux condenser over a boiling water bath. Then the reaction mix was diluted with water to 60 ml, the solution passed through a column with anionite EDE-10P and evaporated until dry in vacuum under nitrogen. 1.39 g VI is obtained with m.p. 235-237°. Yield 95.8% of theoretical. After crystallization 19 ml aqueous acetone (3 vol. acetone, 5 vol. water) 1.06 g VI was obtained with m.p. 239-240°.

Found, %: C 63.88; 64.76; H 10.40; 10.35; N 7.49; 7.59. C₁₀H₁₀O₂N. Calculated, %: C 64.86; H 10.27; N 7.56.

trans- γ -(3-aminocyclohexyl)butyric acid (VII). A solution of 24.31 g V and 158 ml 20% sulphuric acid is heated for 72 hr with a reflux condenser over a boiling water bath. Then the reaction mix is diluted with water to 600 ml, the solution passed through a column with anionite ED-10P and evaporated until dry in a vacuum under nitrogen. 13.36 g VII is obtained with m.p. 213-213.5°. Yield 67.5% of theoretical. After repeated recrystallization from aqueous acetone, 1.54 g VII is obtained with m.p. 228-229°.

Found, %: C 65·15; 63·44; H 10·04; 10·29; N 8·32; 8·05. C₁₀H₁₉O₂N. Calculated, %: C 64.86; H 10·27; N 7·56.

The polycondensation was performed by heating in a nitrogen flow at $230-280^{\circ}$ in glass ampoules with metal sheaths, which were put in apertures in an aluminium block with electrical heating adjustable within $\pm 0.5^{\circ}$.

The melting point of the polymers was determined from the thermochemical curves [13], and also from the disappearance of the birefringence using a polarization microscope with a heatable stand [14]. The melting points as determined by the two methods were the same.

CONCLUSIONS

(1) cis- γ -(3-N-acetylaminocyclohexyl)butyric acid, cis- and $trans-\gamma$ -(3-aminocyclohexyl)butyric acid have been prepared. On the basis of the Auvers-Skitt law and its current interpretation, and on the basis of the fact that the cisisomer is produced in predominant amounts on hydration in acid medium over an effective catalyst, configurations have been ascribed to them.

(2) Polyamides have been prepared on a base of cis- and trans-isomers of γ -(3-aminocyclohexyl)butyric acid.

(3) The properties of the *cis*-isomers of γ -(3- and 4-aminocyclohexyl)butyric acids have been compared and that on *cis*- γ -(3-aminocylohexyl)butyric acid base was found to have a considerably higher melting point, and also forms strong elastic fibres, capable of stretching orientation, from the melt.

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