From the 2,4-dinitrofluorobenzene solution, 2.5 mg. of crystals (m.p. 181°) were isolated which were identified as 2,4-dinitroaniline by mixture melting point with an authentic sample and by its infrared absorption spectrum.

C-Demethyl-N-demethylindolmycin (17) was prepared from guanidine and methyl β-indolylacetate in analogy to similar compounds[12]; crystals from ethanol, m.p. 239–241°. Calcd. for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.33. Found: C, 63.09; H, 4.58; N, 18.36.

Acid Degradation of C-Demethyl-N-demethylindolmycin (17).—Compound **17** (253 mg.) was treated as described for isoindolmycin. The ethyl acetate phase after extraction with carbonate and bicarbonate solution yielded an oil (9 mg.) which showed an infrared absorption band ($CHCl_3$) at 3.45 and 5.76 μ. The 2% sodium bicarbonate fraction contained an oil (28 mg.) that showed infrared absorption at 5.5 (m) and 5.7 (s) μ (dioxane) and was judged to be an impure oxazolidine-2,4-dione. The carbonate solution yielded crystals (218 mg.), m.p. 152–159°; λ_{max} 5.52, 5.75 μ. An analytical sample was obtained from chloroform, m.p. 158–160°. Calcd. for $C_{12}H_{10}N_2O_3$: C, 62.60; H, 4.38; N, 12.17. Found: C, 62.22; H, 4.32; N, 12.03.

Preparation of Racemic α-Indolmycenic Acid (2, R = H).—A mixture of ethyl 2,3-epoxybutyrate[13] (16.1 g.) and indole (16 g.) in carbon tetrachloride (50 ml.) was cooled to −10°. A solution of stannic chloride (33 g.) in carbon tetrachloride (100 ml.) was added over a period of 2 hr. After 1 hr. a reddish gum formed and more solvent (150 ml.) was added. The reaction mixture was stirred with cooling for another hour. Concentrated sodium bicarbonate solution was added until the aqueous layer remained basic. The mixture was filtered and the phases were separated. The organic solution was concentrated to yield an oil (24 g.). This was distilled at 0.3 mm. The fractions boiling below 145° were discarded and those boiling between 145 and 190° (mostly 175°) were collected; 5.45 g. The vapor phase chromatogram indicated the mixture to contain about 9% indole and 80% α-indolmycenic acid ester. The latter v.p.c. fraction was collected and analyzed. The infrared spectrum ($CHCl_3$) was identical with that of α-indolmycenic acid ethyl ester (**2**, R = C_2H_5), prepared from the optically active acid **2** and ethanol in the presence of sulfuric acid. Calcd. for $C_{14}H_{17}NO_3$: C, 67.99; H, 6.93; N, 5.66. Found: C, 68.30; H, 7.05; N, 5.62.

A sample (550 mg.) of the racemic α-indolmycenic acid ester was hydrolyzed in routine fashion and racemic α-indolmycenic acid (**2**, R = H) was obtained; 160 mg., m.p. (from H_2O) 170°. The infrared spectrum (KBr) was very similar to that of the optically active acid **2** (R = H) with slight differences in the 13 μ region. Calcd. for $C_{12}H_{13}NO_3$: C, 65.90; H, 5.98; N, 6.40. Found: C, 65.76; H, 6.00; N, 6.35.

(12) C. F. Howell, N. Q. Quinones, and R. A. Hardy, Jr., *J. Org. Chem.*, **27**, 1679 (1962).

(13) W. D. Emmons and A. J. Pagano, *J. Am. Chem. Soc.*, **77**, 89 (1955).

Preparation of Indolmycin (1) and Isoindolmycin (12).—N,N'-Dimethylguanidine hydriodide (1 g.) was dissolved in 6 ml. of a 0.7 *N* methanolic sodium methylate solution and added to 1 g. of optically active α-indolmycenic acid methyl ester. After standing at room temperature for 1 day, the solution was concentrated to 1 ml. *in vacuo*, 1 *N* hydrochloric acid (10 ml.) was added, and the mixture was extracted three times with 8 ml. of ethyl acetate. The combined organic phases were extracted twice with 10 ml. of water, once with 10 ml. of a 5% sodium bicarbonate solution, and again with 10 ml. of water, then dried over sodium sulfate, filtered, and evaporated *in vacuo* to dryness to yield an oily product (860 mg.). From this on attempted crystallization from ethyl acetate, 20 mg. of crude isoindolmycin (**12**), m.p. 224–230°, identified by infrared absorption spectrum, was isolated. The mother liquor of these crystals was evaporated *in vacuo* to dryness and the residue chromatographed on a column of Woelm aluminum oxide, nonalkaline, grade 1, starting with chloroform as eluent but after 100 ml. had been used, changing gradually to first ethyl acetate and then from ethyl acetate to ethanol, taking fractions of 18 ml. Each second fraction was investigated for its contents of indolmycin by paper chromatography. Indolmycin was eluted by ethyl acetate–5% ethanol and solvent mixtures of higher ethanol content. All fractions showed more than one component. The fractions eluted with ethyl acetate–15% ethanol contained the highest proportion of indolmycin and were investigated further. Direct crystallization from ethyl acetate yielded isoindolmycin, identified by melting point (230–235°) and infrared absorption spectrum. The mother liquor was streaked on untreated Whatman No. 4 paper and chromatographed using 2% aqueous dipotassium phosphate solution as mobile phase. After the chromatogram had been developed, the streak corresponding in R_f value to indolmycin was cut out and eluted with methanol. The methanolic solution was concentrated *in vacuo* to 10 ml., diluted with 100 ml. of ethyl acetate, and extracted twice with 20 ml. of water. The organic phase was dried over sodium sulfate, filtered, and evaporated to dryness. The residue (1.5 mg.) crystallized from ethyl acetate and was washed with ethyl acetate and ether; m.p. 206–209°, on admixture to indolmycin (m.p. 210–213°), m.p. 207–212°. The infrared absorption spectrum (KBr) was identical with that of an authentic sample. The potassium bromide pellet was dissolved in 10 ml. of water. The solution was analyzed by ultraviolet absorption spectrum for indolmycin and by biological assay. Both methods gave identical results of 0.05 mg. of indolmycin per ml.

Acknowledgments.—The authors are greatly indebted to Professor K. Biemann, Massachusetts Institute of Technology, for the determination and interpretation of the mass spectra. Dr. R. L. Wagner and his associates kindly provided the analytical data and physical measurements.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

Optically Active Polyamides. Poly-D(−)-β-methyl-ε-caprolactam[1]

BY C. G. OVERBERGER AND H. JABLONER[2]

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D(−)-β-Methyl-ε-caprolactam has been polymerized to a crystalline polymer melting 90° above the polymer prepared from the racemic monomonomer. A study of the solution properties of poly-D(−)-β-methyl-ε-caprolactam and a model compound, (+)-6-acetamido-3,N-dimethylhexanamide, in mixtures of cresol and chloroform have shown that no ordered helix structure exists, that solvation of the amide carbonyl is independent of polymer conformation, and that each mer is solvated independently. In addition, theories have been presented to explain the changes in λ_c and [η] with solvent composition.

While optically active polymers of α-amino acids have been extensively investigated, optically active polymers other than the poly-α-amino acids have, until recently, received only a small amount of attention.

There have been two principal approaches in the study of optically active polymers. One approach has been concerned primarily with a symmetric induction during polymerization; the second had been concerned with the properties of optically active polymers prepared from optically active monomers. It is only with the second approach that we are concerned here.

In general, optically active polymers have higher melting points and higher crystallinity than their racemic analogs. Examples of this effect are polypropyleneimine,[3] propylene oxide,[4] poly-2-methylbutanal,[5] poly-3-methyl-1-pentene,[6] and polyesters of decamethylene glycol and *d*- and *meso*-tartaric acids.[7] Optically

(1) A preliminary communication on this subject was published: *J. Polymer Sci.*, **55**, 532 (1961).

(2) This paper comprises a portion of the dissertation submitted by H. Jabloner in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

(3) Y. Minoura, M. Takebayashi, and C. C. Price, *J. Am. Chem. Soc.*, **81**, 4689 (1959).

(4) C. C. Price, M. Osgan, R. E. Hughes, and C. Shambelan, *ibid.*, **78**, 690 (1956), and C. C. Price and M. Osgan, *ibid.*, **78**, 4787 (1956).

(5) M. Goodman and A. Abe, *J. Polymer Sci.*, **59**, 537 (1962).

(6) W. J. Bailey and T. T. Yates, *J. Org. Chem.*, **25**, 1800 (1960).

(7) K. W. Doak and H. N. Campbell, *J. Polymer Sci.*, **18**, 215 (1955).

active nylons have been prepared using (+)- and (±)-3-methylhexandoic acids and 1,6-hexanediamine.[8] In this latter case there is structural isomerism in the backbone chain, a type of heterogeneity, but the optically active polyamide was reported to have a slightly higher melting point and density than the racemic polymer.

The optical activity of polymeric solutions has been extensively investigated for poly-α-amino acids primarily in terms of α-helix *vs.* random coil formation.[9]

Optically active polyolefins have been investigated by Bailey[6] and Pino.[10] Bailey reported very high rotations for poly-(+)-3-methyl-1-pentene. The amount of the rotation varied with the solubility of the fractions. The highest rotation of −254° was determined on the crystalline fraction, by dissolving the polymer in boiling 1,1-ditolylethane and measuring the rotation of the small amount of polymer remaining in solution at room temperature. Pino reported a rotation of +194° for poly-(+)-3-methyl-1-pentene in decalin. Pino also reported very high rotations for poly-(−)-4-methyl-1-hexene and poly-(+)-5-methyl-1-heptene. Interpretations of these results was rendered extremely difficult by the poor solubility of these polymers. The high rotations have been attributed to either a small segment of a helical conformation in solution or to molecular association.[10]

Imoto[11] has reported the polymerization of menthone lactam. Because of the presence of the large alkyl substituents of the monomer, it was polymerized at relatively low temperatures with strong catalysts. The maximum intrinsic viscosity attained was only 0.075 dl./g. in formic acid and the rotation in the same solvent was $[\alpha]^{19}D^{-}$ +9.5°. These workers also hydrolyzed the menthone lactam to the corresponding amino acid which had, within experimental error, no optical activity. They interpret the difference between the amino acid and the polyamide as showing "diasymmetric coiling of the polymer molecule." A comparison between the optical rotation of an amino acid and its polyamide is not rigorous because of the difference in the chromophoric group. The exact interpretation of their data is not clear.

Poly-D(−)-β-methyl-ε-caprolactam was selected for this study because of the availability of the monomer, the moderate solubility of the polymer, and the lack of structural isomerism in the polymer because of the method of synthesis. This latter point cannot be overstressed—we are dealing with a structurally homogeneous polymer—a factor which enables one to make reasonable interpretation of the data. Polymers of racemic monomethyl caprolactams have been reported by Schaffler and Ziegenbaum[12]; D(−)-β-methyl-ε-caprolactam was prepared by Wallach[13] starting with D-pulegone.

The hydrolysis of pulegone to give D-3-methylcyclohexanone followed the procedure of Eisenbraun.[14] The preparation of the oxime and Beckmann rearrangement followed the procedure of Wallach.[13] A new procedure was devised for the separation of β-methyl-ε-caprolactam from the mixture of β- and δ-methyl-ε-caprolactam. The more soluble δ-methyl-ε-caprolactam could not be obtained in pure form.

(8) Zh. S. Sogomonyants and M. V. Volkenstein, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*, 623 (1957) (Consultants Bureau English Translation).

(9) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

(10) P. Pino and G. P. Lorenzi, *J. Am. Chem. Soc.*, **82**, 4745 (1960).

(11) M. Imoto, H. Sakurai, and T. Kono, *J. Polymer Sci.*, **50**, 467 (1961).

(12) A. Schaffler and W. Ziegenbaum, *Ber.*, **88**, 1374 (1955).

(13) O. Wallach, *Ann.*, **289**, 337 (1896); **346**, 253 (1906); **309**, 2 (1899).

(14) E. J. Eisenbraun and S. M. McElvain, *J. Am. Chem. Soc.*, **77**, 3383 (1955).

The absolute configuration of the monomer was known, being derived from the known D-configuration of pulegone.[14]

Polymerization of D(−)- and DL-β-Methyl-ε-caprolactam.—Both D(−)- and DL-β-methyl-ε-caprolactam were polymerized using water as an initiator. Data are shown in Table I.

TABLE I

YIELD AND PHYSICAL PROPERTIES OF POLY-D(−)- AND DL-β-METHYL-ε-CAPROLACTAM

Monomer	Water, %	Temp. of polymn., °C.	Time, hr.	Yield, %	[η], dl./g., cresol	M.p., °C.
−	1	230	20	52	0.3	225
±	1	230	20	52	.7	135–145
−	0.5	200	268	80	.96	225
±	0.5	200	268	80	1.3	135–147

Wichterle[15] has reported that for the polymerization of ε-caprolactam the concentration of monomer in equilibrium with the polymer became sharply lower in the vicinity of the polymer melting point. This he interpreted as being due to exclusion of the crystalline polymer phase from the monomer–polymer equilibrium. At a polymerization temperature of 200°, the poly-D-(−)-β-methyl-ε-caprolactam appeared to be a solid mass. Yet the yield of the polymer was identical with that obtained from the racemic monomer which was liquid at 200°. This lack of effect of the solid state, in this case, may be due to the large amount of monomer present which could have plasticized the optically active polymer so that the crystallinity was low despite its solid appearance.

Both racemic and optically active polymer showed X-ray crystallinity.

Solution Properties of Poly-D(−)-β-methyl-ε-caprolactam in Mixtures of Cresol and Chloroform.—Doty and Yang[16] have investigated the rotation of poly-γ-benzyl glutamate in chloroform–dichloroacetic acid mixtures and of silk fibroin insulin, ribonuclease, and bovine serum albumin in ethylene dichloride–dichloroacetic acid mixtures. The curves of specific rotation of poly-γ-benzyl glutamate *vs.* volume per cent of chloroform–dichloroacetic acid mixtures clearly show the onset of helix formation by a discontinuity of the curve. The formation of the helix is also shown by rotatory dispersion measurements.

We have examined the specific rotation and optical rotatory dispersion of poly-D(−)-β-methyl-ε-caprolactam. Helix formation, such as had been proposed by Imoto for polymenthone lactam, could be found by either a discontinuity in the specific rotation *vs.* solvent composition curve or by the dispersion changing from one obeying the Drude equation to one obeying the Moffit equation. The rotations and rotatory dispersions were carried out with two different samples of polymer varying only with respect to molecular weight. Results are given for the lower molecular weight sample in Table II and for the higher molecular weight sample in Table III. Data for the D-line are plotted in Fig. 1 and 2. The curves can be made to coincide by converting volume per cent in Fig. 1 to mole per cent as in Fig. 2. The optical rotatory dispersion curves were found to follow roughly the Drude equation and the λ_c values were calculated from the best straight lines that could be drawn through the data. The dispersions did not follow the Huggins equation. The calculated variations of λ_c with solvent composition are shown in Fig. 3 and Table III. The lack of discontinuity in Fig. 1 and 2 coupled with the rotatory dispersion data

(15) O. Wichterle, *Makromol. Chem.*, **35**, 174 (1960).

(16) J. T. Yang and P. Doty, *J. Am. Chem. Soc.*, **79**, 772 (1957).

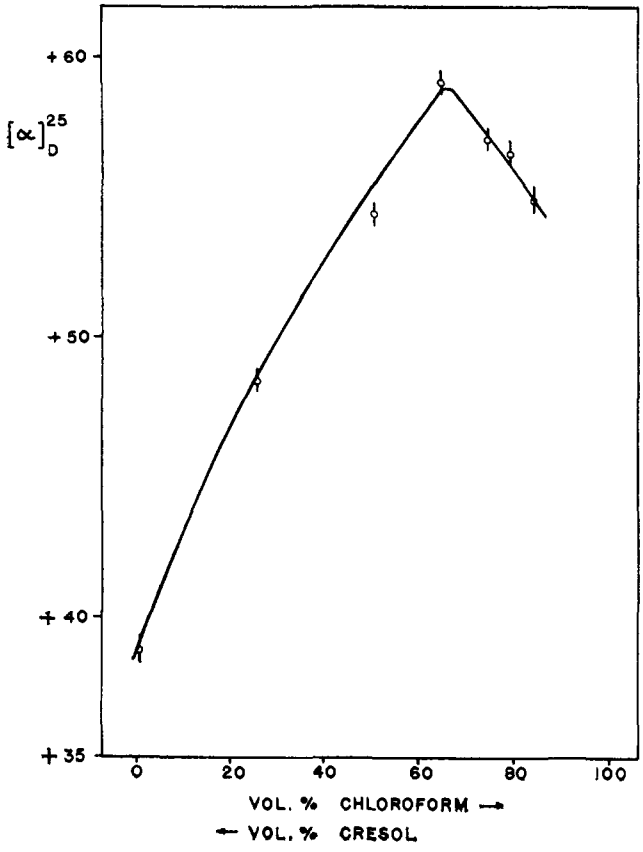

Fig. 1.—The specific rotation of poly-D(−)-β-methyl-ε-caprolactam as a function of solvent composition at 589 mμ.

indicates that, by this criterion, no ordered helix structure exists for major segments of this polyamide.

TABLE II

ROTATION OF POLY-D(−)-β-METHYL-ε-CAPROLACTAM ([η] = 0.30 DL./G., CRESOL) IN MIXTURES OF CRESOL AND CHLOROFORM

Vol. % chloroform	λ, mμ	$[\alpha]^{25}\lambda$	Vol. % chloroform	λ, mμ	$[\alpha]^{25}\lambda$
0	589	39.22	75	589	57.24
	435	88.24		435	118.07
	365	139.71	80	589	56.79
25	589	48.39		546	69.14
	546	56.45		435	118.52
	435	92.74	85	589	55.15
50	589	54.54		546	68.01
67	589	59.30		435	112.13
	546	70.08			
	435	121.29			

A curve of the same general shape as Fig. 2 has been obtained by Tanford, De, and Taggert[17] for solutions of β-lactoglobulin in mixtures of water and organic solvents.

The strong solvent dependence and the existence of a sharp maximum in the specific rotation–solvent composition curve was of sufficient interest that to obtain additional data on the polymer–mixed solvent system (+)-6-acetamido-3,N-dimethylhexanamide was synthesized as a low molecular weight analog of the polymer.

(+)-6-Acetamido-3,N-dimethylhexanamide was synthesized from D(−)-β-methyl-ε-caprolactam by hydrolysis to the corresponding amino acid hydrochloride and conversion of this to (+)-6-amino-3-methylhexanoic acid. The amino acid was acetylated under Schotten–Baumann conditions to give (+)-6-acetamido-3-methyl-

(17) C. Tanford, P. K. De, and V. G. Taggert, *J. Am. Chem. Soc.*, **82**, 6028 (1960).

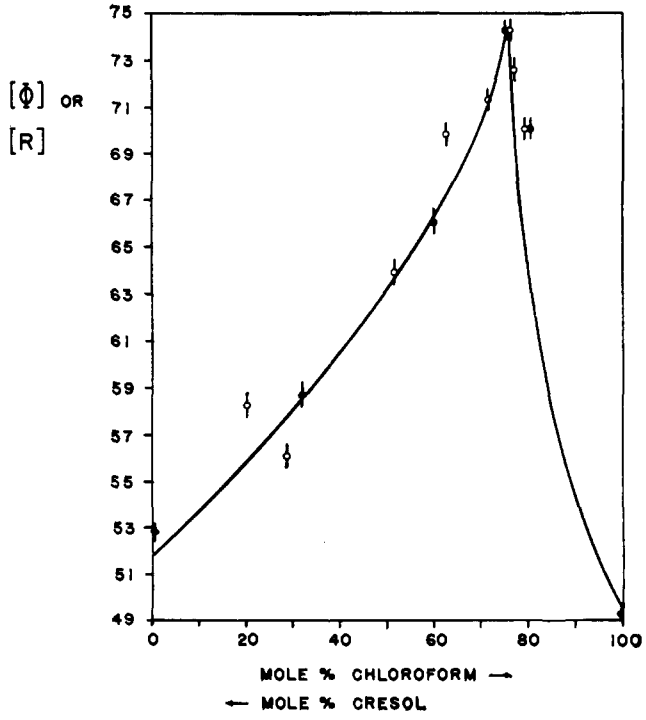

Fig. 2.—The molar rotations of poly-D(−)-β-methyl-ε-caprolactam and (+)-6-acetamido-3,N-dimethylhexanamide as a function of solvent composition at 589 mμ.

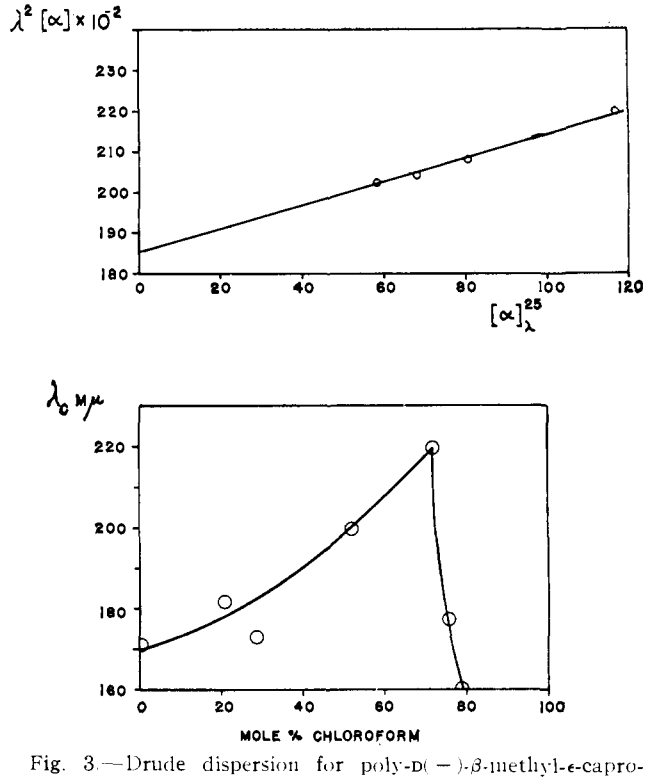

Fig. 3.—Drude dispersion for poly-D(−)-β-methyl-ε-caprolactam (upper curve); critical wave length of poly-D(−)-β-methyl-ε-caprolactam (lower curve).

hexanoic acid. This was then allowed to react with methylamine using the mixed anhydride procedure of Boissonnas[18] to give (+)-6-acetamido-3,N-dimethylhexamide.

Rotations of (+)-6-acetamido-3,N-dimethylhexanamide are shown in Table IV. The mean residue rotation of the polymer and the molar rotation of (+)-6-

(18) R. A. Boissonnas, *Helv. Chim. Acta*, **34**, 874 (1951).

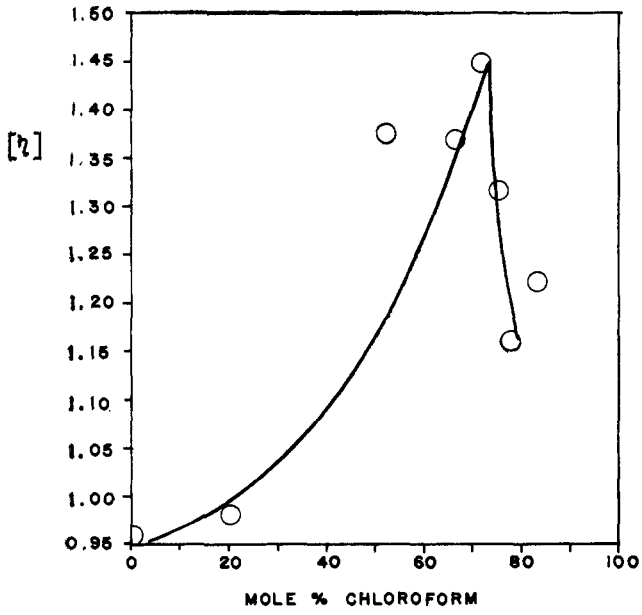

Fig. 4.—Intrinsic viscosity of poly-D(−)-β-methyl-ε-caprolactam in mixtures of cresol and chloroform.

acetamido-3,N-dimethylhexanamide are plotted in Fig. 2. The similarity is obvious.

TABLE III

ROTATION OF POLY-D(−)-β-METHYL-ε-CAPROLACTAM ([η] = 0.96 DL./G., CRESOL) IN MIXTURES OF CRESOL AND CHLOROFORM

Mole % chloroform	λ, mμ	$[\alpha]^{25}D$	$[R]^{25}D$	λ_c, mμ
0	589	39.60	50.37	171
	578	59.52	75.71	
	546	45.63	58.04	
	508.6	53.57	68.14	
	435	77.38	98.43	
20.34	589	45.92	58.41	182
	546	51.02	64.90	
	508.6	61.22	77.87	
29.14	589	44.09	56.08	173
	546	52.10	66.27	
	508.6	66.13	84.12	
	435	88.18	112.16	
52.38	589	50.30	63.98	200
	546	58.35	74.22	
	508.6	68.55	87.20	
	435	98.59	125.41	
62.35	589	54.00	68.69	
71.71	589	56.01	71.24	220
	576	62.24	79.17	
	546	68.46	87.08	
	508.6	78.84	100.28	
	435	116.18	147.78	
75.34	589	58.32	74.18	178
	546	68.61	87.27	
	508.6	80.62	102.55	
	435	116.64	148.37	
77.46	589	57.19	72.75	
	508.6	85.79	109.12	
78.98	589	55.12	79.11	160
	546	64.96	82.63	
	508.6	74.80	95.15	
	435	108.27	137.72	

From the position of λ_c it appears that the optically active chromophore is the amide carbonyl[9] and the variation in its solvation or hydrogen-bonding behavior must be responsible for the observed change in λ_c and $[\alpha]$. This immediately leads to the conclusion that, for this polyamide in this solvent system, solvation of the amide carbonyl is independent of polymer conformation and that each mer is solvated independently.

TABLE IV

ROTATION OF (+)-6-ACETAMIDO-3,N-DIMETHYLHEXANAMIDE IN MIXTURES OF CRESOL AND CHLOROFORM

Mole % chloroform	$[\alpha]^{25}D$	$[\Phi]^{25}D$
0	26.39	52.86
22.24	24.62	49.31
30.25	31.68	63.46
32.62	29.29	58.67
40.78	26.65	53.38
60.24	33.02	66.14
75.54	37.11	74.33
80.19	35.35	70.81
100	24.57	49.21

If the series of dispersion curves describing the optical rotation in the various solvent mixtures are of the same shape, as is the case for the observable part of the curve, any shift in λ_c toward longer wave lengths would result in an increase in $[\alpha]$. An indication that this is actually the case can be seen by comparing Fig. 2 and 3. The difference in position of the maxima shows that some variation of shape does take place. In the following discussion we shall consider that in general an increase in $[\alpha]D$ occurs because of a shift of λ_c to higher wave lengths.

If we consider the addition of cresol to a chloroform solution of an amide, there is an increase in solvent polarity and the initially free amide carbonyl is rapidly hydrogen bonded.[19] Thus for the addition of the first amount of cresol there are two carbonyl species present: the free and the hydrogen-bonded species. The increasing solvent polarity would be expected to change the position of the ultraviolet absorption maximum of both of these species. Pimentel[20] considers the formation of the hydrogen bond to be a stronger influence on shifts in absorption maxima. After the addition of a sufficient amount of cresol the carbonyl would be essentially completely hydrogen bonded. This point should roughly correspond to the maximum in the λ_c *vs.* $[\alpha]$ curve. As still more cresol is added the increasing solvent polarity shifts λ_c for the hydrogen-bonded amide species to lower wave lengths. A decrease in dipole moment for the excited state, relative to the ground state, would be expected to have this effect.[21]

Viscosity of Poly-D(−)-β-methyl-ε-caprolactam in Mixtures of Cresol and Chloroform.—The viscosity of poly-D(−)-β-methyl-ε-caprolactam is shown in Table V and Fig. 4. From the values of k' and of $(\varkappa)$ it appears that the mixed solvent is a better solvent than pure cresol despite the polar nature of the polymer.

TABLE V

INTRINSIC VISCOSITIES AND HUGGINS CONSTANT, k', FOR POLY-D(−)-β-METHYL-ε-CAPROLACTAM IN MIXTURES OF CRESOL AND CHLOROFORM

Mole % chloroform	dl./g.	k'
0	0.960	0.93
20.34	0.980	.61
52.38	1.375	.18
66.87	1.372	.18
71.71	1.447	.18
75.34	1.316	.17
77.46	1.160	.43
83.52	1.227	.17

(19) G. C. Cannon, *Mikrochim. Acta*, 555 (1955).
(20) G. C. Pimentel, *J. Am. Chem. Soc.*, **79**, 3323 (1957).
(21) N. S. Bayliss and E. G. McRay, *J. Phys. Chem.*, **58**, 1002 (1954).

Similar results have been reported for solutions of 6-nylon in cresol to which toluene was added.[22]

These results may be qualitatively explained in terms of ideas developed from the optical rotatory dispersion studies. In order for nylon to dissolve in *m*-cresol essentially all of the amide carbonyls must be hydrogen bonded to cresol to break down the large intermolecular forces in the crystal. However, once the material had dissolved, the conformation of the polymer is determined by methylene group conformation since polar forces have been reduced by hydrogen bonding. Thus the addition of a low cohesive energy density, relatively nonpolar, solvent would be expected to expand the polymer coil. This effect would continue until either the cohesive energy density of the hydrogen-bonded polymer was matched by the mixed solvent or the hydrogen bonding to solvent was decreased by a dilution effect. In either case a maximum is expected.

Experimental

a. Separation of a β-Methyl-ε-caprolactam from the Reaction Mixture.—The distilled lactam mixture was prepared by the procedure of Wallach.[13]

Distilled lactam mixture, 30 g., was dissolved in 340 ml. of ether and 135 ml. of petroleum ether (b.p. 38–40°) added to precipitate 4.6 g. of material, m.p. 96–102°. The precipitated material was dissolved in a minimum amount of boiling *n*-hexane and the *n*-hexane was allowed to cool very slowly to room temperature (if cooling is too rapid an impure product results). Repetition of this recrystallization gave 3.0 g. of D(−)-β-methyl-ε-caprolactam, m.p. 105–106°, $[\alpha]^{25}D$ −36.15° (*c* 1.04, water) [prepared by the same general procedure; m.p. 105–106°, $[\alpha]^{25}D$ −36°].

b. Polymerization of β-Methyl-ε-caprolactam.—Dried monomer was placed in a tube and the tube attached to a vacuum manifold through a standard joint. The tube was evacuated to 0.05 mm. and flushed with nitrogen. A second tube containing the desired amount of water was placed on the manifold, the water was frozen, and the system evacuated. The water was then transferred by cooling the monomer tube and allowing the water tube to warm. The monomer tube was then filled with nitrogen to a pressure of 1 atm. and sealed. The sealed tube was heated by the vapors of a liquid of an appropriate boiling point (quinoline = 230°, acetophenone = 200°). After the polymerization period the tube was opened, the polymer dissolved in anhydrous formic acid, precipitated into water, and dried under vacuum to constant weight. The melting point of the racemic polymer was 135–145° (m.p.[12] 145). The optically active polymer had a melting point of 220–225°, $[\alpha]^{25}D$ +39.7° (*c* 5, cresol).

Anal. Calcd. for $C_7H_{13}NO$ (for optically active polymer): C, 66.09; H, 10.32; N, 11.01 Found: C, 65.93; H, 10.12; N, 11.07.

c. (+)-6-Amino-3-methylhexanoic Acid.—D(−)-β-methyl-ε-caprolactam (17 g., 0.13 mole) was dissolved in a mixture of 60 ml. of water and 60 ml. of concentrated hydrochloric acid and refluxed for 8 hr. The solution was then cooled and the water and excess acid removed in a rotatory evaporator. The brown oil which remained crystallized on cooling to −78° and warming to room temperature. The solid material was dissolved in 50 ml. of water and passed through a column containing 130 g. of Amberlite IR45 resin in a 1-in. diameter column according to the procedure of Meyers and Miller.[23] The material was eluted with 750 ml. of water and the water removed under vacuum. The residue was dissolved in a minimum amount of boiling ethanol and precipitated with ether; 17.5 g., 89%, $[\alpha]^{25}D$ +13.1° (*c*, 1.145, water). The material decomposed at approximately 200°. The infrared spectrum showed peaks at 2375, 2200, 1635, 1570, and 1400 cm.$^{-1}$.

Anal. Calcd. for $C_7H_{15}NO_2$: C, 57.89; H, 10.43; N, 9.65. Found: C, 57.96; H, 10.83; N, 9.43.

d. (+)-6-Acetamido-3-methylhexanoic Acid.—The general procedure used was that of Chattaway[24] for the preparation of N-acetylglycine.

6-Amino-3-methylhexanoic acid (17.5 g., 0.121 mole) was dissolved in 25 ml. of water, and to this solution was added 12.08 g. (0.303 mole) of sodium hydroxide. The solution was cooled in an ice bath and 61 g. of ice was added. Acetic anhydride (15.4 g., 0.151 mole) was then added, all at once, while the flask was shaken vigorously. The ice melted almost immediately and a small additional amount of ice was added. The material was allowed to stand at room temperature for 0.5 hr. and was then acidified with 1 *N* hydrochloric acid. The solvent was removed under vacuum and the residue extracted with 250 ml. of boiling ethyl acetate. Removal of the ethyl acetate gave a white crystalline residue which was dissolved in 166 ml. of ethyl acetate, filtered, and 184 ml. of carbon tetrachloride added to give 17 g. (77%) of the desired product, m.p. 67–69, $[\alpha]^{25}D$ +11.6° (*c* 1.06, ethyl acetate). The infrared spectrum showed peaks at 3370, 2900, 2500, 2000, 1700, 1605, 1560 and 1280 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{17}NO_3$: C, 57.72; H, 9.17; N, 7.48. Found: C, 57.43 H, 8.93; N, 7.56.

e. (+)-6-Acetamido-3,N-dimethylhexanamide.—The procedure followed was similar to that used by Boissonnas[18] for the preparation of a phthalimidoacetamide.

(+) 6-Acetamido-3-methylhexanoic acid (5 g., 0.0268 mole) was dissolved in 35 ml. of dry chloroform and the solution cooled to 0° under nitrogen. Triethylamine (2.71 g., 0.0268 mole), which had been distilled from acetic anhydride and stored over molecular sieves, was added. To this well-stirred solution was added 2.88 g. (0.0268 mole) of ethyl chloroformate. The solution was stirred at 0° for 15 min. and dry methylamine was bubbled in for 30 min. The addition of 200 ml. of ether gave a flocculent white precipitated which was filtered, dissolved in 30 ml. of water, and the solution made alkaline with 1 *N* sodium hydroxide. The alkaline solution was continuously extracted with chloroform for 8 hr. Removal of the chloroform gave 4 g. (74%) of the desired product. Three recrystallizations from ethyl acetate reduced the yield to 2.9 g. (54%) of pure material, m.p. 118–119°, $[\alpha]^{25}D$ +24.57° (*c* 0.46, chloroform). The infrared spectrum showed absorption maxima at 3300, 2900, 1634, 1555, and 1290 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{20}N_2O_2$: C, 59.96; H, 10.08; N, 13.98. Found: C, 59.69; H, 9.70; N, 13.82.

Pptical Rotations.—Rotations were measured with a Rudolph Model 70 polarimeter with a Rudolph photoelectric attachment. The instrument was equipped with sodium, mercury, cadmium, and thallium lamps and by use of these lamps and appropriate filters, light of various wave lengths could be obtained. Measurements were made on solutions in 2-dm. tubes with the temperature controlled to 25.0 ± 0.1° by circulating constant temperature water through the trough on the instrument.

Viscosities.—Intrinsic viscosities were measured in a series of Ubbelohde viscometers with capillary diameters selected to give flow times of 100 sec. or more for the solvents. The viscometers contained coarse sintered glass disks attached just below the reservoir so that solutions were filtered as the liquid was raised into the capillary. The temperature was maintained at 25 ± 0.03°.

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