Optically Active Polyamides, Polymers of 3-, 4-, 5-, and 6-Methyl-7-aminoheptanoic Acids

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ABSTRACT: Optically active poly-(*R*)-3-methyl-7-heptanamide, poly-(*S*)-4-methyl-7-heptanamide, poly-(*R*)-5-methyl-7-heptanamide, and poly-(*R*)-6-methyl-7-heptanamide have been prepared from the corresponding amino acids or lactams. The polymers were all crystalline and their respective melting points were above 175°. The fiber identity periods of the polymers were found to be significantly shorter than that of unsubstituted poly-7-heptanamide. The optical rotatory dispersions of methyl-substituted poly-7-heptanamides in *m*-cresol and in trifluoroethanol obeyed a single-term Drude equation.

A number of studies concerned with the synthesis and characterization of optically active polymers have been undertaken, mainly in the past decade.[2] Among these, synthetic polypeptides and proteins have been extensively investigated. However, relatively little has been reported on optical rotatory dispersion studies of synthetic asymmetric polymers other than polypeptides. In the present study, linear, optically active, methyl-substituted poly-7-heptanamides were prepared and their physical properties were determined.

Earlier attempts[3a] to prepare polyamides from 1,6-diamino-1,6-dideoxy-2,4:3,5-di-O-methylene-D-mannitol and dibasic acids were unsuccessful owing to the high temperature necessary for the conventional melt polycondensation. However, Bird, *et al.*,[3b] prepared high molecular weight, optically active polyamides from carbohydrate derivatives by use of interfacial polycondensation techniques.

Brewster[4] prepared optically active polyamides by the condensation of *meso*-, (±)-, and (+)-α,α'-dimethyladipic acids with hexamethylendiamine.

Optically active polyamides of (±)- and (+)-3-methyladipic acids and hexamethylenediamine have been also prepared by Sogomonyants and Volkenstein.[5] Although there is a structural isomerism (head and tail) in the repeating unit, the melting point of the optically active polymer was reported to be higher than that of the racemic polymer.

Minoura and his coworkers[6] have prepared optically active, low molecular weight polyamides by the condensation of (+)-tartaric acid with diamines.

An optical active poly-(β-amino acid) of L-aspartic acid has been prepared by Balasubramanian.[7] A possible ordered helical structure of the polymer was claimed on the basis of optical rotatory dispersion studies.

Imoto and his coworkers[8] have polymerized menthone lactam (4-methyl-7-isopropyl-2-oxohexamethylenimine). The molecular weight of the polymer was very low because of the severe steric hindrance of the side chains.

Overberger and Jabloner[9] have synthesized a high molecular weight poly-D-(−)-β-methyl-ϵ-caprolactam. The polyamide had a melting point significantly higher than that of its racemic counterpart. Other optically active isomeric C-methylcaprolactams were also polymerized by Overberger and Parker.[10] The optically active polymers were all crystalline and had higher melting points than the racemic polymers. The work was extended to optically active C-methyl-7-nylons. The polymers, unlike even-carbon nylons, were expected to have a different type of crystalline structure[11] due to a different orientation of hydrogen bonds.

Monomers. The complete syntheses of the monomers (*R*)-(−)-4-methyl-2-oxoheptamethylenimine, (*R*)-(−)-7-methyl-2-oxoheptamethylenimine, (*R*)-(+)-7-amino-5-methylheptanoic acid, and (*S*)-(−)-7-amino-4-methylheptanoic acid have been described in another paper.[12] The materials were all prepared from an optically pure starting material, D(+)-pulegnone (2-isopropylidene-5-methylcyclohexanone).

Polymerization. The results of the polymerization of the lactams and amino acids are listed in Table I.

The lactams were polymerized by heating in a sealed tube at 220° in the presence of 1% water. The heat of polymerization of enantholactam is known to be about 2 kcal/mole greater than that of caprolactam.[13] This is attributed mainly to the greater ring strain of enantholactam.[14] Therefore, the conversion for the water-

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(1) Taken from part of the Ph.D. thesis of T. T., 1966.

(2) See the following reviews: R. C. Schulz and E. Kaiser, *Advan. Polymer Sci.*, **4**, 236 (1965); P. Pino, *ibid.*, **4**, 393 (1965).

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TABLE I
YIELD AND PHYSICAL PROPERTIES OF POLY-(C-METHYL-7-HEPTANAMIDE)S

Substitution	Monomer	Yield, %	Mp,[a] °C	$[\eta]$,[c] dl/g	$[\alpha]^{25}\text{D}$[c]
None	Lactam	99.5	226–228[b]	0.86	. . .
(*R*)-3-Methyl	Lactam	82.7	177–179	0.74	+7.51
(*S*)-4-Methyl	Amino acid	93.8	175–176	1.16	+7.55
(*R*)-5-Methyl	Amino acid	90.8	181–182	1.43	+5.09
(*R*)-6-Methyl	Lactam	70.4	186–188	0.83	−6.49

[a] Determined by use of a polarizing microscope with an electrically heated hot stage. [b] Lit. mp 223°.[11] [c] Measured in *m*-cresol.

catalyzed polymerization of enantholactams was significantly higher than was found for caprolactams.

In the polymerization of enantholactam, the concentration of monomer in equilibrium with the polymer is far smaller than that in polymerization of caprolactam.[15] Therefore, the melt polycondensations of 7-aminoheptanoic acids under vacuum were successfully carried out without loss of the monomers by the formation of the corresponding lactams. The polycondenstions were relatively fast and resulted in high molecular weight polymers in high yield.

Crystalline Melting Point. Despite the introduction of a side group, all the optically active polymers derived from the C-methyl-7-heptanamides were crystalline as evidenced by the X-ray diffraction diagrams, and the melting points were relatively high because of the stereoregularity of these polymers.

It is known that racemic C-methyl-substituted 6-nylons have significantly lower melting points or exhibit complete destruction of crystallinity.[9,10,16] On the other hand, optically active C-methyl-6-nylons in which the asymmetric carbons have the same configuration throughout the entire polymer chain were all crystalline.[9,10]

The relatively high melting points of the optically active C-methyl-6-nylon and -7-nylons are probably due to a relatively small entropy of fusion caused by the increased stiffness of the polymer chain imposed by the methyl substitution. It appears that the closer the position of the substitution to the amide group, the higher is the melting point of the polymer. In the case of optically active substituted 6-nylons, substitution on the 3 or 6 positions raised the melting point to a value higher than that of unsubstituted 6-nylon.[10] 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.

Crystalline Structure. X-Ray crystallographic studies were carried out for the oriented specimens of the optically active poly-(C-methyl-7-heptanamide)s. Although the structural analysis was not completed, the fiber identity period was determined for each polymer. The results are shown in Table II.

TABLE II
FIBER IDENTITY PERIOD OF POLY-(C-METHYL-7-HEPTANAMIDE)S

Substitution	Fiber identity period, Å
Unsubstituted	9.81
3-Methyl	9.24
4-Methyl	9.43
5-Methyl	9.11
6-Methyl	9.57

The methyl-substituted poly-7-heptanamides have shorter fiber identity periods than that of unsubstituted poly-7-heptanamide (7-nylon).[11] The methylene chains of unsubstituted, aliphatic polyamides usually have a fully extended zigzag conformation in their crystal lattices.[11,17] Introduction of a methyl group, however, should perturb the fully extended zigzag conformation of the polymethylene chain and cause a twisting around one of the carbon–carbon bonds. This would account for the shorter fiber identity periods of methyl-substituted poly-7-heptanamides as compared to that of unsubstituted poly-7-heptanamide. The result is also in accord with that of optically active poly-(*R*)-3-methyl-6-hexanamide investigated by Coiro.[18]

Optical Rotatory Dispersion. Optical rotatory dispersion analysis has been successfully applied to the investigation of the conformation of polypeptides and proteins in solution.[19] It was one of our main purposes to analyze the optical rotatory dispersions of optically active methyl-substituted poly-7-heptanamides.

The optical rotatory dispersion of polypeptides in a random conformation obeys, like many simple low molecular weight compounds, the single-term Drude equation

$$[\alpha]_\lambda = \frac{K}{\lambda^2 - \lambda_c^2} \qquad (1)$$

where $[\alpha]_\lambda$ is the specific rotation at wavelength λ, K is a constant, and λ_c is the wavelength at which asymmetric absorption occurs. However, if an asymmetric macromolecule is in a stable specific conformation in solution, the resulting asymmetry of the whole polymer molecule may contribute to the optical rotation in excess of that due to the asymmetric residue in the chain. Such a system would be described by a higher order equation, such as the Moffit equation for polypeptides in α-helical form.

In the present work, the optical rotatory dispersions

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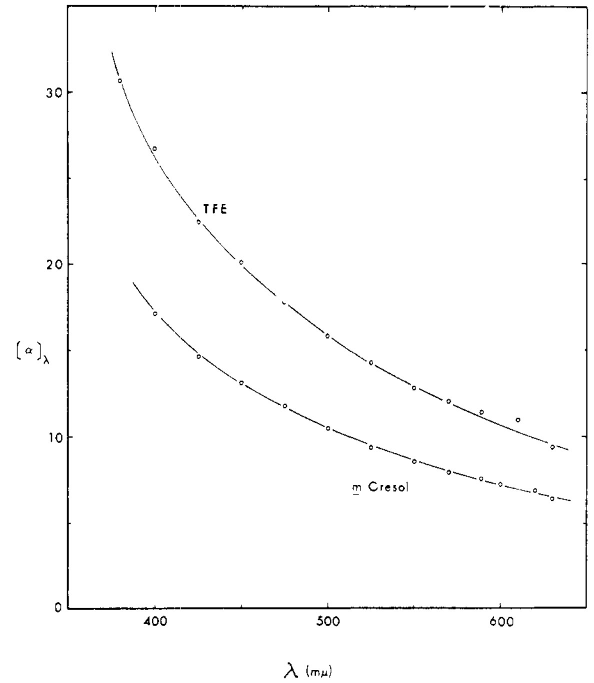

Figure 1. Optical rotatory dispersion of poly-(*R*)-3-methyl-7-heptanamide.

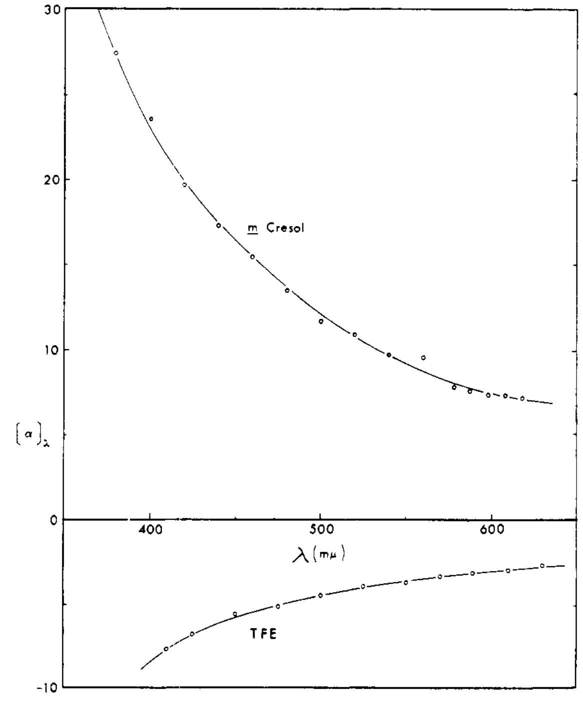

Figure 2. Optical rotatory dispersion of poly-(*S*)-4-methyl-7-heptanamide.

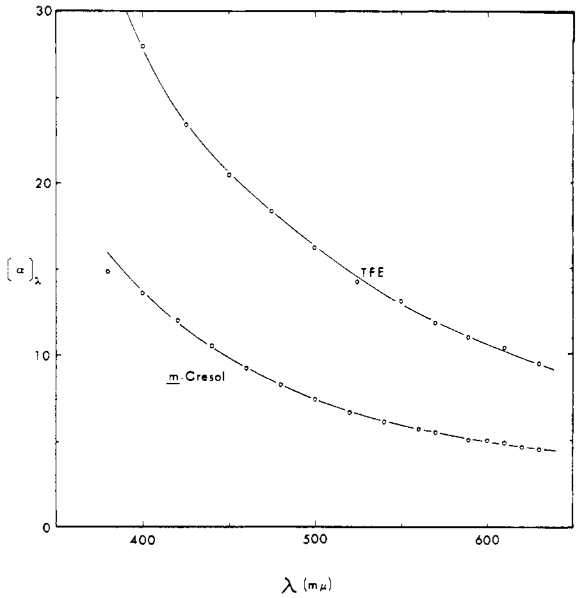

Figure 3. Optical rotatory dispersion of poly-(*R*)-5-methyl-7-heptanamide.

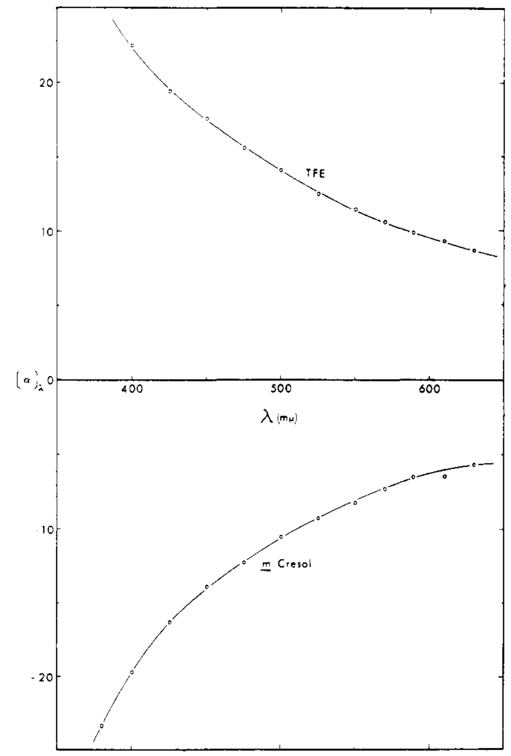

Figure 4. Optical rotatory dispersion of poly-(*R*)-6-methyl-7-heptanamide.

were measured in *m*-cresol and in 2,2,2-trifluoroethanol. The dispersion of poly-(*R*)-3-methyl-7-heptanamide, poly-(*S*)-4-methyl-7-heptanamide, poly-(*R*)-5-methyl-7-heptanamide, and poly-(*R*)-6-methyl-7-heptanamide are shown in Figures 1, 2, 3, and 4, respectively.

Provided that all four polymers were of (*R*) configuration (actually, only the 4-methyl polymer has the (*S*) configuration), the following trend is found. The rotations in 2,2,2-trifluoroethanol were positive for all polymers (positive Cotton effect) and the rotations in *m*-cresol were always smaller than those in 2,2,2-trifluoroethanol. In the case of the 4-methyl and 6-methyl polymers, the rotations in *m*-cresol had negative values (negative Cotton effect). It is interesting to note that there was an alternating effect of substitution on the sign of rotation in *m*-cresol and on the fiber identity period. The substitution of a methyl group on the 3 or 5 position resulted in the same sign of rotation in *m*-cresol and in 2,2,2-trifluoroethanol, whereas 4-methyl or 6-methyl polymer had different signs in the two sol-

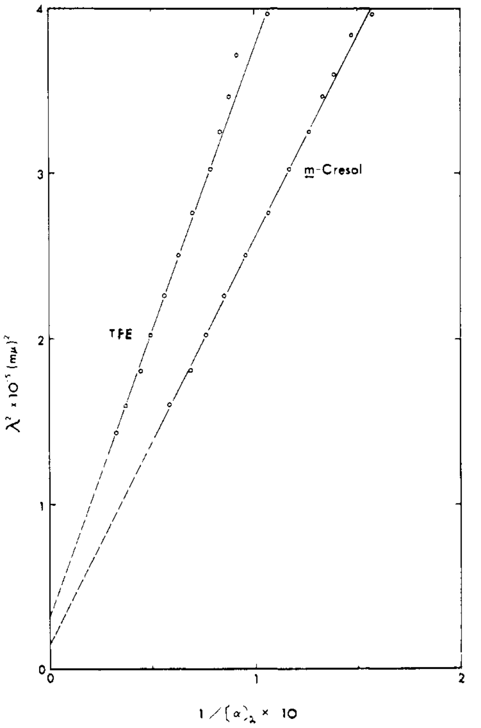

Figure 5. Lowry plot of the ORD of poly-(*R*)-3-methyl-7-heptanamide.

vents. The phenomenon should be attributed to the conformational requirement in the vicinity of the chromophore. A similar effect was also observed for the optical rotatory dispersion of asymmetric aldehydes, (+)-2-methylbutanal, (−)-3-methylpentanal, and (+)-4-methylhexanal.[20]

The Biot–Lowry plot (λ^2 *vs.* $1/[\alpha]$) of the optical rotatory dispersions of poly-(C-methyl-7-heptanamide)s gave a linear relationship as shown in Figures 5–8, indicating that the single-term Drude equation (eq 1) holds in all cases.

The absence of anomaly in the optical rotatory dispersions of poly-(C-methyl-7-heptanamide)s is in accord with the results of poly-(C-methyl-6-hexanamide)s.[9,10] Although these polyamides possess stereospecific structure, their backbone chains may be too flexible to take a "stable specific asymmetric conformation" and cause an anomaly in their optical rotatory dispersions.

The value of Drude constant λ_c was calculated from the intercept of each line in Figures 5, 6, 7, and 8 and listed in Table III. The extremely low values of λ_c were obtained for poly-(*R*)-3-methyl-7-heptanamide and for poly-(*R*)-6-methyl-7-heptanamide. Since the optically active chromophore is the amide carbonyl,[19] the variation in the solvation and hydrogen-bonding behavior of the amide group would be responsible for the large variation of λ_c. It is then understandable that the strongest solvent effect is seen when the amide chromophore is closest to the asymmetric carbon.

Infrared Spectra. Infrared spectra of optically active poly-(C-methyl-7-heptanamide)s were obtained for the film specimens. The spectra are identical except for some minor differences in the 900–1400-cm^{-1} region.

Table III
Drude Constant λ_c of Optically Active Poly-(C-methyl-7-heptanamide)s

Substitution	λ_c, mμ In *m*-cresol	In 2,2,2-trifluoroethanol
3-Methyl	134	173
4-Methyl	239	197
5-Methyl	210	187
6-Methyl	249	118

Experimental Section

A. **Poly-(*R*)-3-methyl-7-heptanamide.** (*R*)-(−)-4-Methyl-2-oxoheptamethylenimine (1.000 g) was placed in a 5-ml polymerization tube and the tube was flushed with nitrogen. Water (10 μl) was added, and the tube was sealed. The polymerization was carried out by heating the tube at 220° for 44 hr. The polymer, an opaque white solid, was dissolved in 98% formic acid and precipitated in water: yield, 0.827 g (82.7%); mp 177–179°; [η] 0.74 dl/g (*m*-cresol, at 25°); $[\alpha]^{25}\text{D}$ +7.51° (*c* 1.77, *m*-cresol), +11.39° (*c* 1.06, 2,2,2-trifluoroethanol).

B. **Poly-(*R*)-6-methyl-7-heptanamide.** (*R*)-(+)-7-Methyl-2-oxoheptamethylenimine (0.650 g) was polymerized under the same conditions as described above, using 6.5 μl of water as a catalyst. The polymer was dissolved in 98% formic acid, precipitated in water, and dried under vacuum: yield, 0.457 g (70.4%); mp 186–188°; [η] 0.83 dl/g (*m*-cresol at 25°); $[\alpha]^{25}\text{D}$ −6.49° (*c* 1.59, *m*-cresol), +9.90° (*c* 1.51, trifluoroethanol).

C. **Poly-7-heptanamide.** 2-Oxoheptamethylenimine was polymerized in the same manner as described above except that polymerization was carried out at 230° for 40 hr. The polymer was dissolved in formic acid and precipitated in water: yield, 99.5%; mp 226–228°; [η] 0.86 dl/g (*m*-cresol, at 25°); mp 223°.[11]

D. **Poly-(*S*)-4-methyl-7-heptanamide.** (*S*)-(−)-7-Amino-4-methylheptanoic acid (0.800 g) was placed in a 5-ml polymerization tube equipped with a side arm and a gas-inlet capillary. Purified nitrogen gas was introduced through the capillary and the tube was heated at 170°. After the monomer had completely melted, the pressure was gradually reduced to 20 mm in 0.5 hr. The temperature was raised to 240° in 0.5 hr at this pressure. Finally, the polymerization was completed by heating at 240° and 0.3 mm for 1.5 hr. During the polymerization, a slow stream of nitrogen was continuously introduced into the polymer melt in order to facilitate the removal of water. The polymer was dissolved in 98% formic acid and precipitated in water: yield, 93.8%; mp 175–176°; [η] 1.16 dl/g (*m*-cresol, at 25°); $[\alpha]^{25}\text{D}$ +7.55° (*c* 1.13, *m*-cresol), −3.18° (*c* 2.55, trifluoroethanol).

E. **Poly-(*R*)-5-methyl-7-heptanamide.** (*R*)-(+)-7-Amino-5-methylheptanoic acid (1.00 g) was polymerized in the same manner as described for (*S*)-(−)7-amino-4-methylheptanoic acid except that the polymerization was carried out at 220° (0.5 mm) for 1 hr and at 240° (0.3 mm) for 2 hr. The polymer was dissolved in 98% formic acid and precipitated in water: yield, 90.8%; mp 181–182°; [η] 1.43 dl/g (*m*-cresol at 25°); $[\alpha]^{25}\text{D}$ +5.09 °(*c* 2.89, *m*-cresol), +11.04° (*c* 1.28, trifluoroethanol).

Polymer Melting Points. The melting points of the polyamides were measured by using a polarizing microscope equipped with an electrically heated hot stage and a thermocouple.

Infrared Spectra. A film of each polyamide was cast from a 2,2,2-trifluoroethanol solution directly on a sodium

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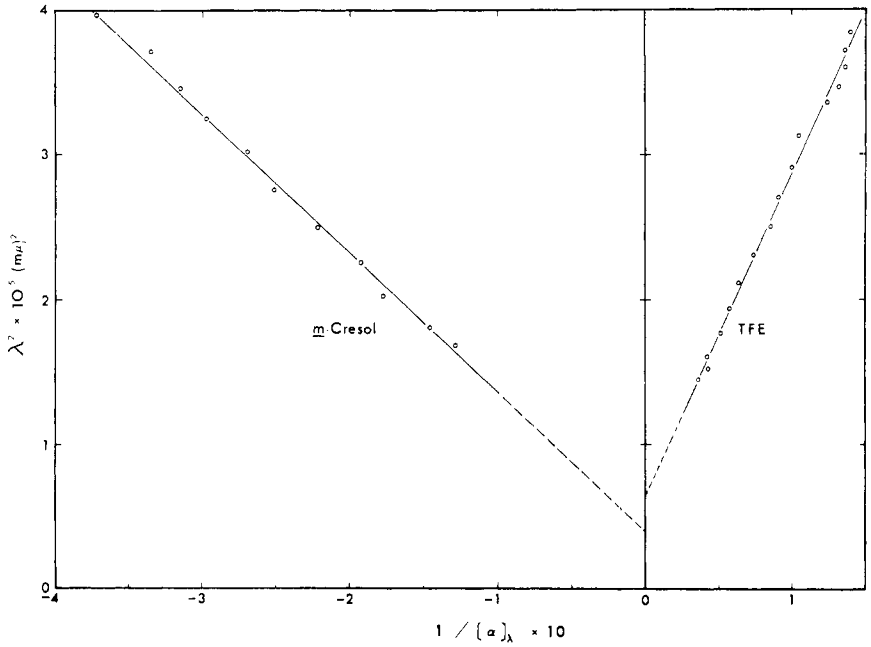

Figure 6. Lowry plot of the ORD of poly-(*S*)-4-methyl-7-heptanamide.

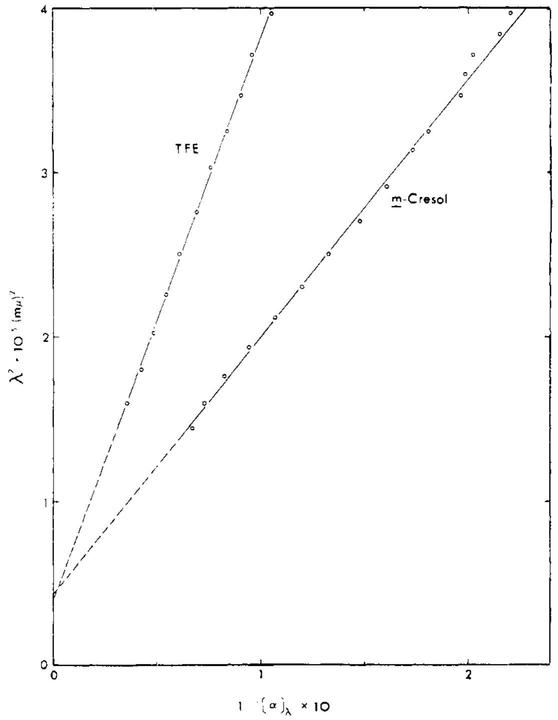

Figure 7. Lowry plot of the ORD of poly-(*R*)-5-methyl-7-heptanamide.

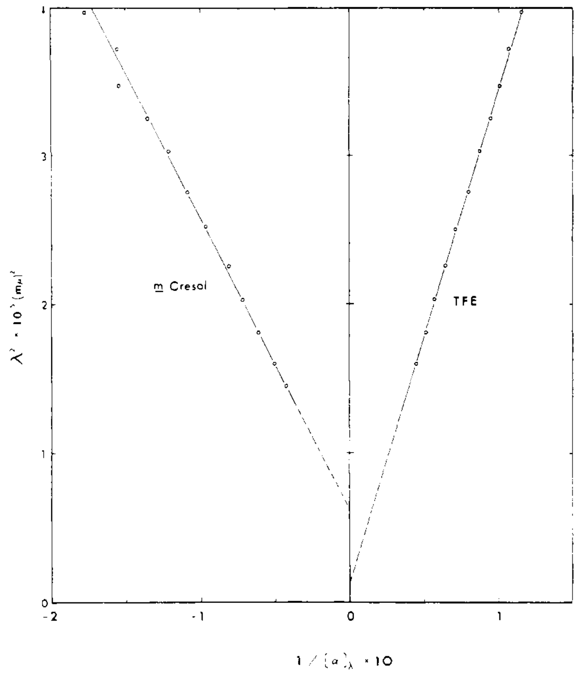

Figure 8. Lowry plot of the ORD of poly-(*R*)-6-methyl-7-heptanamide.

chloride plate. The spectra were measured with a Perkin-Elmer 521 grating infrared spectrophotometer.

X-Ray Diffraction Diagrams. A film of each polyamide was cast from a trifluoroethanol solution. The oriented specimen was prepared by cold drawing of the film strip followed by a heat treatment under load at a temperature 10–50° below the melting point.

Optical Rotation. Optical rotations were measured with a Rudolph Model 70 spectropolarimeter equipped with a xenon lamp as the light source.

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