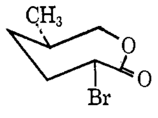
bromine atom both equatorial was the most stable conformer in trifluoroethanol. Here too, a small deformation of the ring is expected to relieve the α–ε proton repulsion. In heptane, the situation is more complicated because of repulsion between the α-bromine and the carbonyl group. Although this energy is only about 0.45 kcal/mole,[34] it is uncertain at this time whether in combination with the α–ε proton repulsion energy, the planarity of the lactone group will be broken.



II

The planar projection of chair ε-caprolactone looking down the carbonyl group shown in Figure 8a summarizes the signs of the n–π* Cotton effects for substituents at the appropriate positions. The enantiomers of the δ-methyl- and α-bromo-δ-methyl lactones are drawn in this diagram. It can be seen that the α-bromine atom falls in the lower left quadrant below the plane of the lactone group. The conclusion which can be drawn from this diagram is that the atoms in the upper and lower left quadrants contribute most to the sign of the Cotton effect, in agreement with the rule of Okuda,[2] Klyne's sector rule,[4,5] and more recently with the modified sector rule.[9] Furthermore, the signs for the atoms in these quadrants are in accord with the theoretical calculations of Schellman[36,37] for the analogous amide group.

The signs of the background Cotton effects, most pronounced for the β- and δ-methyl lactones, Figures 1 and 3, can be summarized in Figure 8b. It is uncertain whether a π–π* or another transition[38,39] is responsible. Diagram 8b is suggestive of a lactone rule for the higher energy transitions.

Experimental Section

Optical rotatory dispersion measurements were taken with a Bendix-Ericcson Polarimatic 62 automatic scanning spectropolarimeter.[40] Dispersions were carried out in 5-, 1-, and 0.1-mm jacketed quartz cells and optical rotations below 40% transmission were ignored. Below 200 mμ a nitrogen flush was used. Rotatory dispersion data are expressed as molar rotations for the lactones. Refractive index corrections were made on all dispersion measurements.[41] For trifluoroethanol the value of the refractive index, n^{25}D 1.2895,[42] was used at all wavelengths. For *n*-heptane, the value $n^{25}{}_{434}$ 1.3938 was used at all wavelengths.[43] All ultraviolet spectra were taken on a Perkin-Elmer Model 350.

Acknowledgments. Acknowledgment is given to Professor Murray Goodman of this department for the use of the Bendix-Ericcson ultraviolet spectropolarimeter and to Dr. A. Felix for carrying out some of the measurements. A sample of iridomyrmecin kindly supplied by Professor Mario Pavan of the Instito di Entomologia Agraria dell Universita di Pavia, Italy, was greatly appreciated.

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[36] J. A. Schellman and P. Oriel, *J. Chem. Phys.*, 37, 2114 (1962).

[37] B. J. Litman and J. A. Schellman, *J. Phys. Chem.*, **69**, 978 (1965).

[38] I. Listowsky, G. Avigad, and S. England, *J. Am. Chem. Soc.*, **87**, 1765 (1965).

[39] I. Listowsky, S. England, and G. Avigad, *Carbohydrate Res.*, **2**, 261 (1966).

[40] R. P. Resnik and K. Yamaska, *Biopolymers*, **4**, 242 (1966). Because of the results reported in the paper cited, our optical rotatory dispersion results may only be qualitatively correct.

[41] G. Fasman, *Methods Enzymol.*, **6**, 928 (1964).

[42] H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, 70, 1281 (1948).

[43] Landolt-Bornstein, "Physikalische Chem. Tabellen," Vol. II, Part 8, Springer-Verlag, Berlin, 1962.

The Optical Rotatory Dispersion and Conformation of Some Poly-ε-caprolactones in Solution

Charles G. Overberger and Howard Kaye[1]

Contribution from the Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York. *Received March 30, 1967*

Abstract: Optically active polymethyl-ε-caprolactones and their model compounds were prepared *via* the lactones. No special conformations were detected for these polyesters in solution as evidenced by the linear decrease in the ratio of the Cotton effect extrema for the β-methyl polymer and its model compound as a function of decreasing coil size and the absence of any $n-\pi_3{}^*$ Cotton effects for the γ-methyl and δ-methyl polymers in good and poor solvents. The Drude equation was obeyed in all solvents studied and the λ_0 values corresponded to those ultraviolet bands which were optically active.

In solution under special conditions polypeptides[2-5] and polynucleotides[6] can exist as extended helices. Recently a great deal of experimental evidence has been presented supporting the existence of microhelical regions in solutions of isotactic polymers.[7,8]

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[1] Taken from the dissertation of H. Kaye submitted to the faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1965.

[2] M. A. Stahman, "Polyamino Acids, Polypeptides and Proteins," The University of Wisconsin Press, Madison, Wis., 1962.

[3] E. R. Blout, *Tetrahedron*, 13, 123 (1961).

[4] J. Tsi Jang, *ibid.*, 13, 143 (1961).

[5] See papers in "Biopolymers," Symposia No. 1, "Quantom Aspects of Polypeptides and Polynucleotides," M. Weissbluth, Ed., Interscience, Division of John Wiley and Sons, Inc., New York, N. Y., 1964.

[6] J. R. Fresco, *Tetrahedron*, 13, 185 (1961).

[7] M. Goodman, J. Brandrup, and H. F. Mark, "Crystalline Polyolefins," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1965.

It was, therefore, of interest as part of a general program to investigate the detailed conformation in ideal solution of macromolecules which were structurally homogeneous and which were devoid of the complication of internal hydrogen bonding. It was hoped from a study of a material such as this that an insight into the subtle factors which control the detailed conformation of a macromolecular coil might be obtained.

The system selected was the methyl-substituted polyesters derived from the corrresponding optically active ε-caprolactones.[9]

Synthesis

The three optically active lactones described previously[9] were polymerized by a modification of the Korte[10] procedure using an aluminum triisobutyl-water cocatalyst system in a benzene solution at 50°.

Poly-(*R*)-(−)-β-methyl-ε-caprolactone was obtained in 60% yield as a sticky, viscous transparent material, $[\eta]^{25}{}_{\mathrm{TFE}} = 0.92$ dl/g, which was not crystalline at −13° by X-ray diffraction.

Poly-(*R*)-(+)-γ-methyl-ε-caprolactone was also obtained as a sticky, viscous, glassy material in 44.5% yield as $[\eta]^{25}{}_{\mathrm{TFE}} = 0.44$ dl/g. An X-ray diagram at −14° indicated only a minute amount of crystallinity.

Poly-(*R*)-(−)-δ-methyl-ε-caprolactone, however, was obtained as a sticky, viscous, turbid material in 42.5% yield, $[\eta]^{25}{}_{\mathrm{TFE}} = 0.50$ dl/g. After 2 months at room temperature it crystallized into a tough, waxy material melting at 29–30° on the hot-stage polarizing microscope. The *d* spacings are listed in Table I.

Table I. *d* Spacings of Poly-(*R*)-(−)-δ-methyl-ε-caprolactone at 14°

d, A	Intensity[a]	*d*, A	Intensity[a]
4.36	vs	2.89	m
3.78	vw	2.52	m
3.49	w	2.18	Broad w
3.28	m		

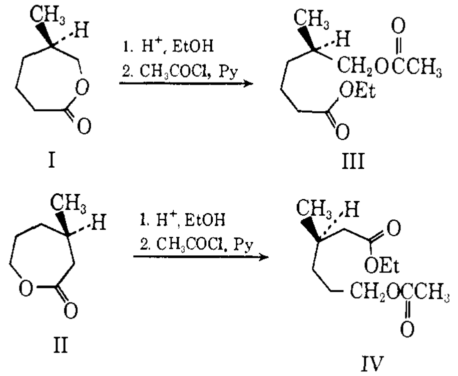
[a] Abbreviations used are: vs, very strong; vw, very weak; w, weak; m, medium.

Racemic γ-methyl-ε-caprolactone was polymerized in bulk yielding 58.2% of the viscous, glassy polyester, $[\eta]^{25}{}_{\mathrm{TFE}} = 0.76$ dl/g.

Although all of the above polymerizations were carried out under the same conditions, variations in the yields and intrinsic viscosities can be seen. This is probably due to the experimental error associated with the sensitivity of the polymerization to the ratio of water to aluminum triisobutyl.

It is also interesting to note that because poly-ε-caprolactone[11] melts at 53–55° it can be concluded that the effect of an asymmetric center along the backbone of a polyester with a seven-atom repeating unit is to reduce the melting point of the polyester and that as the asymmetric center gets further from the carbonyl group the decrease is less.

(*R*)-(−)-δ-Methyl-ε-caprolactone (I) and (*R*)-(−)-β-methyl-ε-caprolactone (II) were converted into their corresponding model compounds by acid-catalyzed alcoholysis at 25° in a closed system to the hydroxy esters followed by acetylation with acetyl chloride in pyridine. Thus (*R*)-(+)-ethyl 6-acetoxy-5-methylhexanoate (III) and (*R*)-(+)-ethyl 6-acetoxy-3-methylhexanoate (IV) were obtained in 71.3 and 35.5% yield, respectively.



I III

II IV

Optical Rotatory Dispersion and Conformation of Polyesters in Solution

In order to investigate the detailed conformation of the optically active polymethyl-substituted ε-caprolactones in solution, the experimental approach selected was to vary the size of the macromolecular coil by the proper selection of thermodynamically good, ideal, and poor solvents while observing the ultraviolet optical rotatory dispersion in the region of the Cotton effect. In a good solvent, the macromolecular coil would be expanded thereby decreasing the chances of any special conformations, such as folds or microhelices, whereas in ideal or θ solvents, the unperturbed dimensions and conformation of the chain would be controlled by short-range forces[12a] and polymer–polymer medium range forces, thus increasing the probability of forming these special conformations if they could exist at all. The conformation in poor solvents or solvents which are thermodynamically below θ would be expected to depend to an increased extent on polymer–polymer interactions which in turn might induce other or similar special conformations as described above. Thus if some special conformation were to form in the ideal or poor solvent the Cotton effect would be expected to change in intensity or sign from that observed in good solvent.

It should be pointed out, however, that special conformations such as short sequences of *n*/1 helices of one sense where *n* is a large number of mers, probably cannot be detected by ultraviolet rotatory dispersion because the asymmetry produced by the helix would be extended over too large a volume of space for the chromophores to see it. Long-range conformations such as this can probably only be detected by far-infrared or microwave rotatory dispersion. Tinoco[12b] has used microwave rotatory dispersion and observed a Cotton

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(8) W. R. Krigbaum, "New Methods of Polymer Characterization," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1964.

(9) C. G. Overberger and H. Kaye, *J. Am. Chem. Soc.*, **89**, 5646 (1967).

(10) V. H. Chendron, H. Ohse, and F. Korte, *Makromol. Chem.*, **56**, 179, 187 (1962).

(11) F. J. Natta, J. W. Hill, and W. H. Carothers, *J. Am. Chem. Soc.*, **56**, 455 (1934); **58**, 183 (1936).

(12) (a) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 424; (b) I. Tinoco and M. P. Freeman, *J. Phys. Chem.*, **61**, 1196 (1957).

Table II. Intrinsic Viscosity of Polyesters

Solvent	β-Methyl	γ-Methyl	(±)-γ-Methyl	δ-Methyl
TFE	0.92 ± 0.01	0.44 ± 0.01	0.76 ± 0.01	0.50 ± 0.01
Dioxane	0.60 ± 0.01	0.30 ± 0.01	0.49 ± 0.01	0.35 ± 0.01
t-Amyl alcohol	0.37 ± 0.01	0.16 ± 0.01	0.32 ± 0.01	0.20 ± 0.01

Table III. Solubility Parameters of Solvents

Solvent	Hildebrand solubility parameter
TFE	14.9 ± 1[a]
Dioxane	9.732[14]
t-Amyl alcohol	10.15[15]

[a] Determined from pressure–temperature data.

Table IV. Optical Rotatory Dispersion of Poly-(*R*)-(−)-β-methyl-ϵ-caprolactone and Its Model Compound

Solvent at 25°	λ_p, mμ	λ_m, mμ	$[m']_p$[a]	$[m']_m$[a]	$[m']_p/[m']_m$
TFE	221 ± 1	221 ± 1	660 ± 12	640 ± 25	1.03 ± 0.06
Dioxane	226 ± 1	226 ± 1	340 ± 11	406 ± 21	0.85 ± 0.06
t-Amyl alcohol	224 ± 1	224 ± 1	320 ± 12	430 ± 16	0.75 ± 0.055

[a] Subscript p refers to polymer. Subscript m refers to model compound.

effect for macroscopic copper helices of one sense as an example of this.

As an additional method for detecting special conformations and solvation effects, the optical rotatory dispersion measurements for the polymers were compared with those for the corresponding model compounds in the same solvents. A comparison with the optical rotatory dispersion properties of the lactones[9] was also made, as the lactones can be considered to be good models for a helix.

The solubility properties of poly-(+)-γ-methyl-ϵ-caprolactone were determined in order to select suitable solvents for this study. Solvents were screened on the basis of solubility and spectral purity, while the final selection was made from intrinsic viscosity measurements. Mixed solvents were not used in this study in order to avoid additional solvation problems.

Trifluoroethanol, dioxane, and *t*-amyl alcohol met the desired solvent requirements. Tables II and III show the intrinsic viscosities of all the polyesters in each of these solvents and the solubility parameters, respectively, and it can be qualitatively seen that trifluoroethanol is a good solvent whereas dioxane and *t*-amyl alcohol become increasingly worse.

Although it is uncertain if dioxane is a medium or ideal solvent, the *t*-amyl alcohol is thought to be approximately a Θ or below Θ solvent because the polyester precipitates from it at −6° at a concentration of 0.477 g/100 ml. The intrinsic viscosities of all the polyesters have been plotted against the Hildebrand solubility parameter[13] as shown in Figure 1. While these polyesters should have solubility parameters of about 8 or 9, it is usual in structurally similar polymer–solvent systems for the solvent with the same solubility parameter as the polymer to exhibit a maximum value of the intrinsic viscosity, whereas solvents with different solubility parameters show smaller intrinsic viscosities. The relationship has been found to be Gaussian.[13]

Thus the intrinsic viscosities in going from *t*-amyl alcohol to dioxane increase while the solubility parameter of the solvent approaches that of the polymer, as shown in Figure 1. Because of the high solubility parameter of trifluoroethanol, the intrinsic viscosity would be expected to be quite small. The fact that it is as large as it is indicates very strong interaction, most likely hydrogen bonding, with the polyesters.

The optical rotatory dispersion curves of poly-(*R*)-(−)-β-methyl-ϵ-caprolactone and its model compound, (*R*)-(+)-ethyl 6-acetoxy-3-methylhexanoate, are shown in trifluoroethanol, Figure 2, dioxane, Figure 3, and *t*-amyl alcohol, Figure 4. It can be seen that a positive

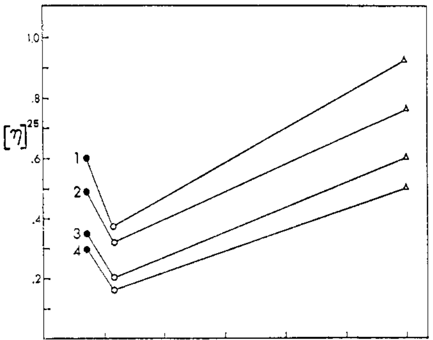

Figure 1. Intrinsic viscosities of polyesters *vs.* the Hildebrand solubility parameter: 1, poly-(*R*)-(−)-β-methyl-ϵ-caprolactone; 2, poly-(±)-γ-methyl-ϵ-caprolactone; 3, poly-(*R*)-(−)-δ-methyl-ϵ-caprolactone; 4, poly-(*R*)-(+)-γ-methyl-ϵ-caprolactone; solvents: ●, dioxane; ○, *t*-amyl alcohol; Δ, tetrafluoroethanol.

n–π_3* Cotton effect peak occurs at 221 mμ for trifluoroethanol, 226 mμ for dioxane, and 224 mμ for *t*-amyl alcohol, consistent with the solvent dependency of an n–π_3* transition.[14] The dispersion data are tabulated in Table IV.

The most significant result of these measurements is the fact that as the solvent becomes poorer, the difference in the rotation at the peak of Cotton effect between the model compound and polyester increases as shown in Figures 2, 3 and 4, and Table IV. The intensity of rota-

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(13) D. Mangara, S. K. Bhatnagar, and S. B. Roth, *Makromol. Chem.*, **67**, 75 (1963).

(14) (a) W. D. Closson and P. Haug, *J. Am. Chem. Soc.*, **86**, 2384 (1964). (b) This is probably due to the interaction or complexation of the solvent molecules with the chromophore thereby affecting the electric moment. (c) With only three points it would be difficult to distinguish between a first- and second-order transition.

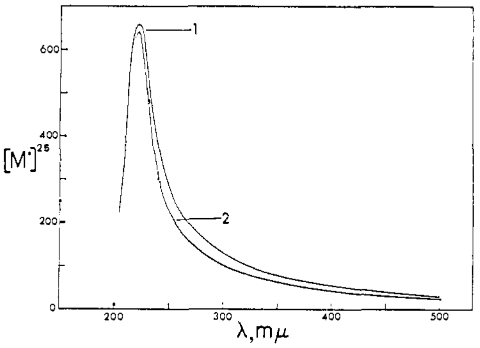

Figure 2. Optical rotatory dispersion curves of poly-(*R*)-(−)-β-methyl-ε-caprolactone and its model compound in tetrafluoroethanol: 1, β-methyl polymer; 2, β-methyl model compound.

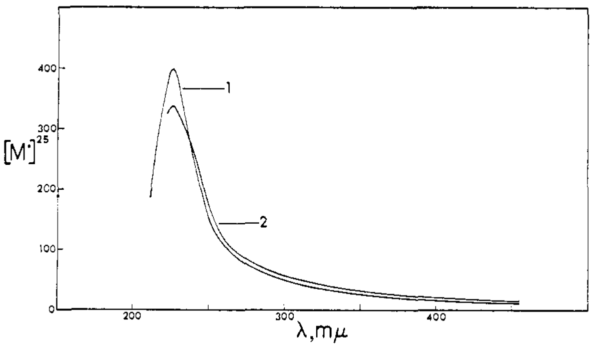

Figure 3. Optical rotatory dispersion curves of poly-(*R*)-(−)-β-methyl-ε-caprolactone and its model compound in dioxane: 1, β-methyl model compound; 2, β-methyl polymer.

tion of the model compound can also be seen to decrease dramatically in the order of decreasing hydrogen bonding ability of the solvent, analogous to the effect of solvent on the rotations of the lactones.[9,14b] A quantitative comparison of the rotations in different solvents cannot be made because of the unknown refractive indices at low wavelength and the additive effect of the solvent-sensitive $\pi-\pi_3{}^*$ Cotton effect. The ratio of the mean residue rotation of the polymer and model compound in their respective solvents can be compared quantitatively however, because the refractive index correction cancels out while the position of the λ_{max} remains the same. By plotting this ratio *vs.* the intrinsic viscosity of the polyester, a straight line within experimental error was obtained, as shown in Figure 5. It is a reasonable assumption, as first-order approximation, that the conformation of the model compound is not affected by solvent. If this is so then the linear decrease in the ratio of rotation of the polymer over that of the model compound as a function of decreasing coil size indicates that no special first- or second-order[14c] polymer conformational transitions have occurred, which suggests that the polyester in solution under ideal conditions exists as a random coil. In order to gain a semiquantitative understanding of this result we must examine the Rosenfield equation.[15]

$$R = \mu_m\mu_e \cos\theta \quad (1)$$

where R = rotational strength, μ_m = magnetic dipole moment, μ_e = electric dipole moment, and θ = angle between electric and magnetic dipole moments. Since

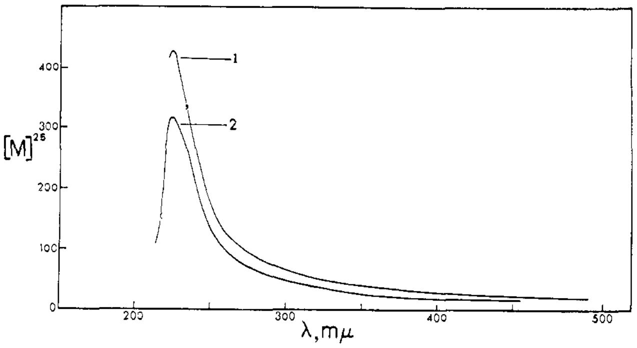

Figure 4. Optical rotatory dispersion curves of poly-(*R*)-(−)-β-methyl-ε-caprolactone and its model compound in *t*-amyl alcohol: 1, β-methyl model compound; 2, β-methyl polymer.

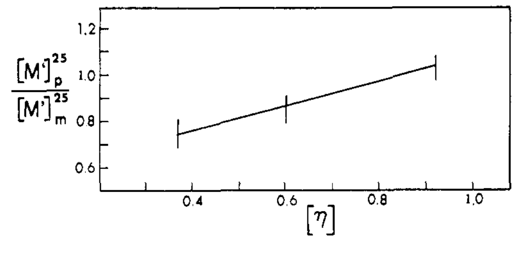

Figure 5. Plot of the ratio of the mean residue rotations of poly-(*R*)-(−)-β-methyl-ε-caprolactone and its model compound *vs.* intrinsic viscosity.

optical rotation is directly related to the rotational strength,[15] the ratio of rotation of the polymer over that of the model compound can be written

$$\frac{[m']_p^{25}}{[m']_m^{25}} = \frac{\mu_{mp}\mu_{ep}\cos\theta_p}{\mu_{mm}\mu_{em}\cos\theta_m} \quad (2)$$

where the subscripts p and m refer to the polymer and model compound, respectively.

Since the electric dipole moment is related to the dipole strength of an electronic transition[15]

$$D \approx \mu_e^2 \quad (3)$$

where D = dipole strength and μ_e = electric dipole moment, then

$$\mu_{ep}/\mu_{em} = (D_p/D_m)^{1/2} \quad (4)$$

The ratio of the dipole strength of the polymer over that of the model compound is recorded in Table V

Table V. Ultraviolet Absorption Data for Poly-(*R*)-(−)-β-methyl-ε-caprolactone and Its Model Compound

Solvent at 25°	$\lambda_{max,p}$, mμ	$\lambda_{max,m}$, mμ	ϵ_p	ϵ_m	$D_p/D_m{}^b$
TFE	209	209	83.0 ± 2	96.4 ± 12	0.89 ± 0.04
Dioxane	215[a]	215[a]	72.0 ± 2	85.5 ± 2	0.91 ± 0.04
t-Amyl alcohol	210	210	78.6 ± 2	88.4 ± 2	0.89 ± 0.05

[a] λ at which sample began to cut out. [b] The actual dipole strengths of these materials were not determined; the ratios were determined from the areas of the curves down to the λ_{max} or λ cut out.

and plotted *vs.* the intrinsic viscosity of the polyester in Figure 6. It can be seen that this ratio remains constant within experimental error at various coil sizes. The value of 0.9 is reasonable as the model compound is

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[15] S. F. Mason, *Quart. Rev.* (London), 17, 20 (1963).

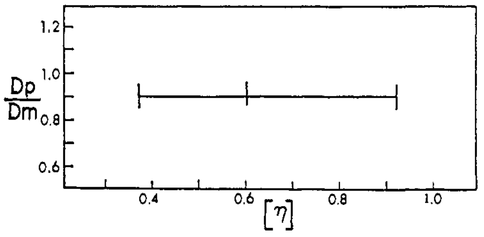

Figure 6. Plot of the ratio of the dipole strengths of poly-(*R*)-(−)-β-methyl-ε-caprolactone and its model compound *vs.* intrinsic viscosity.

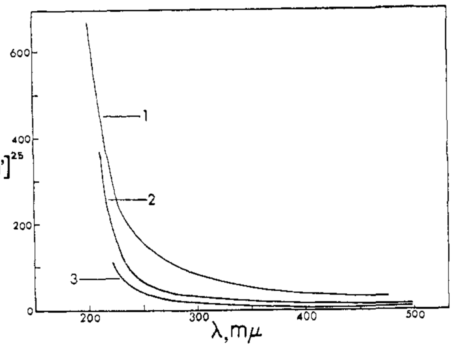

Figure 7. Optical rotatory dispersion curves of poly-(*R*)-(+)-γ-methyl-ε-caprolactone in tetrafluoroethanol, 1, dioxane, 2, and *t*-amyl alcohol, 3.

not an exact model of the polymer. If we then assume that μ_m is the same for the polyester and the model compound in analogy to the constancy of μ_m in unsaturated ketones[15] then

$$\mu_{mp}/\mu_{mm} = \text{constant} \tag{5}$$

Because the conformation of the model compound remains the same $\cos \theta_m$ is also constant. By combining constants in eq 2 we arrive at the following result[16]

$$[m']_p^{25}/[m']_m^{25} = K \cos \theta_p \tag{6}$$

where K = constant.

Relating this to the linear relationship shown in Figure 5 gives us eq 7 where c and b are constants.

$$\cos \theta_p = c[\eta] + b \tag{7}$$

From this equation it can be seen that as the macromolecular coil decreases in size the average angle between the magnetic and electric moments increases. The change is probably due to the increase in the flexibility or conformational mobility of the random coil as it approaches ideal conditions, thereby increasing the average θ_p.

That the results obtained above are not an artifact due to association of the polymer can be ruled out because the $[\eta]_{sp}/c$ *vs.* c curves were very linear over the concentration range used for the optical rotatory dispersion measurements. Association of the model compound in the various solvents has not been experimentally disproven but it is felt that such a situation would be unlikely due to the polar nature of the solvents.

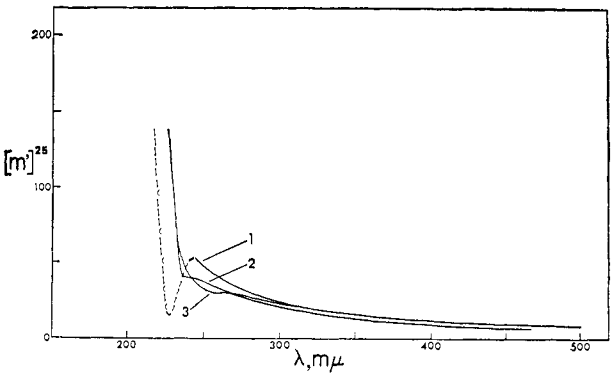

Figure 8. Optical rotatory dispersion curves of poly-(*R*)-(−)-δ-methyl-ε-caprolactone in tetrafluoroethanol, 1, dioxane, 2, and *t*-amyl alcohol, 3.

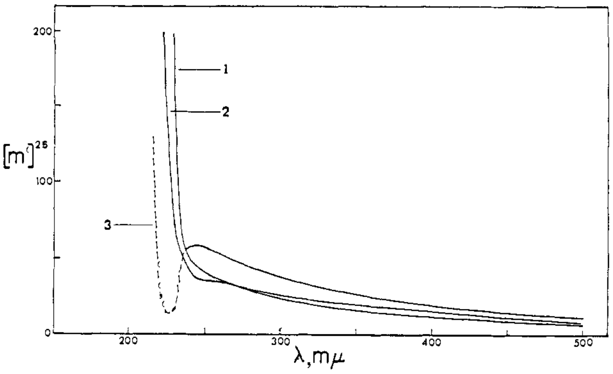

Figure 9. Optical rotatory dispersion curves of (*R*)-(+)-ethyl 6-acetoxy-5-methylhexanoate in dioxane, 1, *t*-amyl alcohol, 2, and tetrafluoroethanol, 3.

For poly-(*R*)-(+)-γ-methyl-ε-caprolactone, it can be seen in Figure 7 that an n–π_3* Cotton effect can no longer be seen in any of the solvents. Apparently the asymmetric carbon is too far away from the carbonyl to have any effect on the orbitals. Nevertheless, one of the π–π_3* Cotton effects can be seen to be positive while the same order of rotational strength as already shown for the β-methyl polymer in the three solvents was also observed.

Figure 8 shows the dispersion curve of poly-(*R*)-(−)-δ-methyl-ε-caprolactone in the same three solvents. Although the mean residue rotation scale has been doubled in Figure 8, the small rotations observed for this polymer further emphasize the effect of having an asymmetric carbon atom three atoms away from the carbonyl group. Very similar dispersion curves are shown for (*R*)-(+)-ethyl 6-acetoxy-5-methylhexanoate, the model compound in Figure 9. Because the rotations were so small for these materials, the low signal-to-noise ratio greatly increased the experimental error of these measurements. In the vicinity of 250 mμ where the rotations increased slightly, the same rotational strength solvent dependency as mentioned above could be detected, although the differences are in the range of experimental error. For the materials in trifluoroethanol, a dashed line is shown at low wavelengths, indicating that a weak negative Cotton effect may be present, but the noise level was so high that we cannot be certain.

Unfortunately, a comparison of the rotation of the polymer and model compound cannot be made because

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(16) A referee has pointed out that a good deal of the intensity of the n–π* transition may be vibrationally induced, which would not contribute to the rotational strength. The importance of this and its effect on the above analysis require further study.

of the same reasons. Despite the large error, the dispersions of the polymer and model compound in dioxane and *t*-amyl alcohol were very similar.

Both the β-methyl polymer and γ-methyl polymers obeyed the Drude equation in all solvents studied. The δ-methyl polymer followed the Drude equation but the scatter, due to reasons mentioned above, was so great that an accurate determination of the Drude constants was unattainable. The data for poly-(*R*)-(−)-β-methyl-ε-caprolactone and poly-(*R*)-(+)-γ-methyl-6-caprolactone listed in Table VI were determined using the mean residue rotations corrected for refractive index.

Table VI. Drude Constants for Poly-(*R*)-(−)-β-methyl-ε-caprolactone and Poly-(*R*)-(+)-γ-methyl-ε-caprolactone

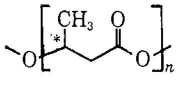
Solvent	β-Methyl polymer K_p	β-Methyl polymer λ_c, mμ	γ-Methyl polymer K_p	γ-Methyl polymer λ_c, mμ
TFE	6.45×10^6	203 + 5	5.2×10^6	166 ± 5
Dioxane	2.40×10^6	220 ± 5	1.78×10^6	185 ± 5
t-Amyl alcohol	2.38×10^6	203.5 ± 5	1.0×10^6	176 ± 5

From Table VI, it can be seen that λ_c for the β-methyl polymer corresponds quite well with the n−π_3* absorption bands obtained from the ultraviolet studies in Table V. For the γ-methyl polymer, there was no n−π_3* Cotton effect, and the λ_c measured corresponds to the π−π_3* transition, as expected. Although the λ_c values gave only an approximate wavelength for the absorption maximum associated with a Cotton effect, it nevertheless is a useful parameter for determining which ultraviolet transition is responsible for the optical rotatory properties far from the particular Cotton effect. In addition, the λ_c value is also sensitive enough, at least qualitatively, to detect wavelength shifts due to solvent as evidenced in Table VI.

From the Drude results and from the results obtained with the β-methyl polymer and its model compound described above, along with the fact that no respectable n−π_3* Cotton effect could be observed in poor solvent for the γ- and δ-methyl polyesters in contrast to that of the corresponding lactones,[9] and the fact that no inversion of sign of any Cotton effect was seen, a conclusion is reached that there are probably no dramatic conformational changes such as microhelix or fold formation occurring in poor solvent which are important enough to be detected by ultraviolet rotatory dispersion.

Studies on a natural occurring polyester, poly-β-hydroxybutyrate (V), which is a three-carbon lower homolog of the polymethyl-ε-caprolactones, have suggested that the solid-state conformation is helical.[17]

The simplest optically active polyester, poly-(*S*)-lactic acid, has also been studied[18] in solution. No positive evidence of secondary structure has been reported.



V

Experimental Section

1. **General.** Optical rotatory dispersion measurements were carried out as already described,[9] except that rotatory dispersion data are expressed as mean residue rotations[19] for the polymers and molar rotations for the model compounds. Refractive index corrections were made on all dispersion measurements. For trifluoroethanol the value $n^{25}\text{D}$ 1.2895[20] was used at all wavelengths. The value $n^{25}{}_{265.6}$ 1.4699[19] was used at all wavelengths for spectral grade dioxane. Spectral grade *t*-amyl alcohol was prepared by hydrogenating the commercial material in a Parr bottle with platinum oxide and 3 atm of hydrogen for 24 hr followed by distillation. The value of $n^{25}\text{D}$ 1.4026 was used at all wavelengths for the *t*-amyl alcohol. All ultraviolet spectra were taken on a Bausch and Lomb 505 using freshly prepared solutions, and all infrared analysis was carried out on Perkin-Elmer Models 21 and 521 infrared spectrophotometers.

Intrinsic viscosity measurements were taken with closed system Cannon-Ubbelohde semimicroviscometers in which the solvent flow times were never less than 100 sec. A constant temperature bath was maintained at ±0.005°, and all flow times were reproducible to ±0.1 sec. All solvents and solutions were filtered through microfritted glass filters before being placed in the viscometer. Pipets were calibrated with all solvents used. Four concentrations ranging from 0.5 g/100 ml to 0.2 g/100 ml were generally employed. All melting points are corrected and all boiling points are uncorrected. Microanalyses were carried out by Alfred Bernhardt Microanalytiches Laboratorium, Mülheim (Ruhr), Germany.

2. **General Polymerization Procedure.** A modification of the procedure of Chendron, Ohse, and Korte[10] was used. The lactone (0.95 g, 0.0074 mole) was placed in a dry polymerization tube containing a rubber serum cap and a calcium chloride drying tube under dry nitrogen. To this was added 0.08 ml of 0.974 *N* solution of aluminum triisobutyl in benzene (7.8×10^{-5} mole), followed by 0.93 mg (5.16×10^{-5} mole) of water (water:aluminum = 0.66) and 5 ml of dry reagent grade benzene. The mixture was cooled to −75° and the tube sealed and placed in a 50° bath for 14 hr. At the end of this time the solution was highly viscous and clear. Upon opening the cooled tube the polymer was precipitated three times from ethanol or methanol at 5° with benzene as solvent. The viscous glassy liquid polymer was then dissolved in benzene, filtered through a medium fritted-glass filter, freeze dried, and dried at 100° (0.1 mm) for 24 hr.

3. **Poly-(*R*)-(−)-β-methyl-ε-caprolactone.** The general procedure described above was used. From 0.95 g (0.0074 mole) of (*R*)-(−)-β-methyl-ε-caprolactone,[9] $[\alpha]^{25}\text{D}$ +32.18° (*c* 1.24, $CHCl_3$), $n^{25}\text{D}$ 1.4583, was obtained 0.57 g (60%) of poly-(*R*)-(−)-β-methyl-ε-caprolactone as a viscous glassy material which became slightly cloudy at −10°. An X-ray diagram at −13° showed little crystallinity, broad band *d* = 10.4 A (weak), d_2 = 4.62 A (strong), $[\eta]^{25}{}_{\text{TFE}}$ = 0.92 ± 0.01 dl/g, $[\alpha]^{25}{}_{450}$ +32.57° (*c* 0.482, TFE). Its infrared spectrum (Figure 1) exhibited carbonyl absorption typical of an ester at 1735 cm^{-1}.

Anal. Calcd for $(C_7H_{12}O_2)_n$: C, 65.59; H, 9.44. Found: C, 64.41; H, 9.31; ash, 1.492; after subtracting the ash: C, 65.38; H, 9.38.

4. **Poly-(*R*)-(+)-γ-methyl-ε-caprolactone** was prepared by the general procedure described above.

From 0.95 g (0.0074 mole) of (*R*)-(+)-γ-methyl-ε-caprolactone,[9] $[\alpha]^{25}\text{D}$ +51.77° (*c* 3.46, $CHCl_3$), was obtained 0.423 g (44.5%) of poly-(*R*)-(+)-γ-methyl-ε-caprolactone as a viscous glassy material which did not crystallize on cooling. An X-ray diagram at −14° indicated only two broad halos, *d* = 7.7 A (weak), d_2 = 4.7 A (strong), $[\eta]^{25}{}_{\text{TFE}}$ = 0.44 ± 0.01 dl/g, $[\alpha]^{25}{}_{450}$ +26.95° (*c* 0.50, TFE). The infrared spectrum (Figure 2) possessed peaks typical of an ester group at 1740 and 1170 cm^{-1}.

Anal. Calcd for $(C_7H_{12}O_2)_n$: C, 65.59; H, 9.44. Found: C, 65.84; H, 9.52; ash, 0.304.

5. **Poly-(*R*)-(−)-δ-methyl-ε-caprolactone** was prepared by the same general procedure described above.

From 2.0 g (0.0156 mole) of (*R*)-(−)-δ-methyl-ε-caprolactone,[9] $[\alpha]^{25}\text{D}$ −36.11° (*c* 0.46, $CHCl_3$), 0.188 ml of 0.838 *N* aluminum triisobutyl in benzene (15.62×10^{-5} mole) and 0.93 mg (5.16×10^{-5} mole) of water (water:aluminum = 0.33) and 5 ml of benzene was obtained 0.85 g (42.5%) of poly-(*R*)-(−)-δ-methyl-ε-caprolac-

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[17] R. Alper, D. G. Lundgren, R. H. Marchessalt, and W. A. Cote, *Biopolymers*, **1**, 545 (1963).

[18] R. C. Schulz and J. Schwaab, *Makromol. Chem.*, **87**, 90 (1965); M. Goodman and M. D'Alagni, *J. Polymer Sci.*, *B*, **5**, 515 (1967).

[19] C. D. Fasman in "Methods in Enzymology," Vol. VI, S. P. Colowick and N. O. Kaplan, Ed., Academic Press Inc., New York, N. Y., 1963, pp 928, 956.

[20] H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, 70, 1281 (1948).

tone as a viscous cloudy liquid, $[\eta]^{25}_{\mathrm{TFE}} = 0.50 \pm 0.01$ dl/g. After 2 months at room temperature, the polyester crystallized into a tough white waxy material, mp 29–30°, by the hot-stage polarizing microscope. An X-ray diagram at −14° indicated sharp lines and a high degree of crystallinity (see Table I for *d* spacings); $[\alpha]^{25}_{450}$ +8.78° (*c* 1.068, TFE). The infrared spectrum of this material showed the characteristic absorption of an ester group at 1740 and 1170 cm^{-1}.

Anal. Calcd for $(\mathrm{C_7H_{12}O_2})_n$: C, 65.59; H, 9.44. Found: C, 64.62; H, 9.40; ash, 1.143; after substracting the ash: C, 65.37; H, 9.43.

6. **Poly-(±)-γ-methyl-ε-caprolactone.** The same general procedure described above was used except that aluminum triisobutyl was added as the pure liquid and the polymerization run in bulk. From 5.2 g (0.041 mole) of (±)-γ-methyl-ε-caprolactone,[9] 0.15 g (7.58×10^{-4} mole) of aluminum triisobutyl, and 9 mg (5×10^{-4} mole) of water was obtained 3.03 g (58.2%) of poly-(±)-γ-methyl-ε-caprolactone as a viscous glassy material, $[\eta]^{25}_{\mathrm{TFE}} = 0.76 \pm 0.01$ dl/g. The infrared spectrum of this material was identical with that of poly-(*R*)-(+)-γ-methyl-ε-caprolactone.

Anal. Calcd for $(\mathrm{C_7H_{12}O_2})_n$: C, 65.59; H, 9.44. Found: C, 65.01; H, 9.18; ash, 1.154; after subtracting the ash: C, 65.64; H, 9.39.

7. **(*R*)-(+)-Ethyl 6-Acetoxy-5-methylhexanoate (III).** (*R*)-(−)-δ-Methyl-ε-caprolactone,[9] $[\alpha]^{25}_{\mathrm{D}}$ −36.11° (*c* 0.46, $\mathrm{CHCl_3}$), 1.0 g (0.0078 mole), was allowed to stand for 3 days at room temperature in 35 ml of ethanol saturated with hydrogen chloride. The ethanol and hydrogen chloride were then removed under vacuum. To the remaining oil, 10 ml of ether, 5 ml of pyridine, and 3 g of acetyl chloride in 5 ml of ether were added, and the resulting mixture was stirred and refluxed overnight. At the end of this time, 10 ml of water was added, and the ethereal phase was extracted with cold 10% sulfuric acid followed by saturated sodium bicarbonate solution. After drying over molecular sieves for 12 hr, the ether was removed on a rotating evaporator and the remaining oil distilled through a microdistillation apparatus yielding 1.2 g (71.3%) of (*R*)-(+)-ethyl 6-acetoxy-5-methylhexanoate, bp 81° (0.2 mm), $[\alpha]^{25}_{350}$ −15.91° (*c* 0.314, TFE), n^{25}_{D} 1.4283.

Anal. Calcd for $\mathrm{C_{11}H_2O_4}$: C, 61.09; H, 9.32. Found: C, 61.08; H, 9.32. The infrared spectrum showed the characteristic ester absorptions at 1740 (s) and 1240 cm^{-1} (s).

8. **(*R*)-(+)-Ethyl 6-Acetoxy-3-methylhexanoate (IV).** The same procedure as for (*R*)-(+)-ethyl 6-acetoxy-5-methylhexanoate was used.

From (*R*)-(−)-β-methyl-ε-caprolactone,[9] $[\alpha]^{25}_{\mathrm{D}}$ −32.18° (*c* 1.24, $\mathrm{CHCl_3}$), n^{25}_{D} 1.4583, 1 g (0.0078 mole), was obtained 0.6 g (35.5%) of (*R*)-(+)-ethyl 6-acetoxy-3-methylhexanoate, bp 84° (0.2 mm), $[\alpha]^{25}_{350}$ +29.78° (*c* 0.460, TFE), n^{25}_{D} 1.4294.

Anal. Calcd for $\mathrm{C_{11}H_{20}O_4}$: C, 61.09; H, 9.32. Found: C, 61.09; H, 9.38.

The infrared spectrum showed the characteristic ester absorptions at 1740 (s) and 1240 cm^{-1} (s).

Acknowledgment. Acknowledgment is given to Professor Murray Goodman of this department for the use of the Bendix-Ericcson ultraviolet spectropolarimeter.

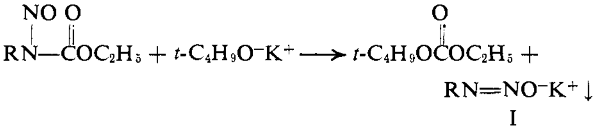
The Solvolysis of Alkyl Diazotates. II. Stereochemistry and Internal Return in the 2-Octyl System[1]

Robert A. Moss and Stuart M. Lane

Contribution from Wright Laboratory, School of Chemistry, Rutgers, The State University, New Brunswick, New Jersey 08903. *Received April 25, 1967*

Abstract: The deamination of optically active 2-octylamine in aqueous nitrous acid affords racemic 2-octanol. Active 2-octylamine was converted to octane-2-diazotate by a series of reactions believed to preserve optical purity. Decomposition of the active diazotate in aqueous base afforded 2-octanol with 16% net inversion. Hydrolysis in the presence of ether (or pentane) afforded 2-octanol with 46% (38%) net inversion. Under either purely aqueous or ether–water conditions, acidic hydrolysis of the diazotate afforded more completely racemized alcohol. Hydrolysis of the diazotate in $\mathrm{H_2O^{18}}$ showed that *ca.* 40% of the derived 2-octanol had retained the original diazotate oxygen; for hydrolysis under ether–water conditions, the corresponding datum was *ca.* 38%. The extent of hydride-shifted (3- and 4-) octanols was determined for the various deaminations, and was largest for nitrous acid deamination of the amine. Hydrolysis of the active diazotate under ether–water conditions showed little stereochemical response to increasing hydroxide ion concentration. The results are discussed in terms of octane-2-diazotic acid as an important intermediate in the diazotate hydrolysis. In such reactions, it is suggested that a free 2-octyl cation is largely bypassed. In the presence of acid, it is suggested that much diazotic acid escapes to free diazonium and/or carbonium ions. The deamination (aqueous nitrous acid, pH 4) of active 2-butyl- and α-phenylethylamines was reinvestigated during the course of this work. The principal product was, in each case, the corresponding alcohol, formed with 22 and 14% net inversion, respectively.

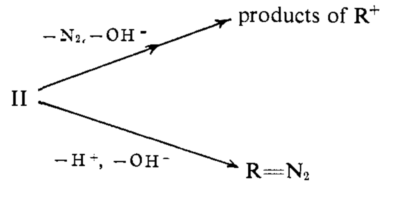
We have recently shown that N-alkyl-N-nitrosourethans are cleaved to alkyl diazotates (I) by the action of ethereal potassium *t*-butoxide (eq 1).[1]



$$\mathrm{R\overset{NO}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}OC_2H_5} + t\text{-}\mathrm{C_4H_9O^-K^+} \longrightarrow t\text{-}\mathrm{C_4H_9O\overset{O}{\overset{\|}{C}}OC_2H_5} + \underset{\mathrm{I}}{\mathrm{RN{=}NO^-K^+}}\downarrow \qquad (1)$$

Hydrolysis of the diazotates occurs almost instantaneously in aqueous base, affording diazoalkanes and/or nitrogen and products commonly associated with carbonium ions (eq 2 and 3). Partition of the diazotic acid

$$\mathrm{RN{=}NO^-K^+ + H_2O \rightleftharpoons \underset{II}{RN{=}NOH} + K^+OH^-} \qquad (2)$$



(3)

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[1] Part I: R. A. Moss, *J. Org. Chem.*, **31**, 1082 (1966).