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Conformation and Moffitt b_0 of Poly(R(-)-propylene oxide) and Poly(R(-)-propylene sulfide)

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LETTER TO THE EDITOR

Conformation and Moffitt b_0 of Poly(R(+)-propylene oxide) and Poly(R(+)-propylene sulfide)

The sign of optical rotation of poly(R(+)-propylene oxide) (poly(R(+)-PO)) is known to be plus in the chloroform solution and minus in the benzene solution [1]. We are studying the details of this phenomenon and we reported recently [2] on the conformation of poly(R(+)-PO). From the analyses of optical rotatory dispersion (ORD) of the solutions and dipole moment of the polymer in the solutions, as well as ORD of the polymer films, we concluded that poly(R(+)-PO) takes a gauche form around the methylene-methine bond, as shown in Fig. 1, to form a helix as a whole, in a local sense, in both cyclohexane and chloroform solutions.

The polymerization of propylene oxide by anionic catalyst, e.g., KOH or $ZnEt_2$ -methanol, takes place mainly with retention of the asymmetric configuration of α -carbon through the ring opening between β -carbon and oxygen (β -opening) [3]. Therefore, if we take the more stable one between the two gauche forms for the conformation of the monomer unit in poly(R(+)-PO), then the most likely conformation of the polymer will be a right-handed helix. The sign of the observed b_0 of the Moffitt equation was minus for poly(R(+)-PO), as expected.

Tsunetsugu et al. [4] reported the ORD data of poly(S(-)-propylene sulfide) (poly(S(-)-PS)). We found an interesting correspondence between poly(R(+)-PO) and poly(R(+)-PS)*.

Our analyses of their data on poly(S(-)-PS) showed that the ORD data of poly(S(-)-PS) both in chloroform and benzene solutions did not fit Drude plots but did closely fit Moffitt plots by assuming $\lambda_0 = 230 \text{ m}\mu$ where ultraviolet absorption was reported for the polymer, and that the sign of Moffitt b_0 was plus for poly(S(-)-PS) both in chloroform and benzene solutions.

The polymerization of S(-)-propylene sulfide by potassium hydroxide was reported to occur also through " β -opening" of the episulfide ring with retention of asymmetric configuration at α -

*Our interpretation is a little different from that of the original authors.

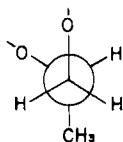


Fig. 1. Gauche conformation (the more stable one).

carbon [4], so that the more stable conformation of the two gauche conformations around methylene-methine bond of poly(S(-)-PS) will lead to a left-handed helix, which seems probable from the observed plus sign of Moffitt b_0 . Therefore, the results of our analysis of the ORD data indicate that poly(R(+)-PS) takes a right-handed helix form, in a local sense, of course, both in chloroform and benzene solutions.

The correspondence between poly(R(+)-PO) and poly(R(+)-PS) is summarized in Table 1.

It is well known that poly(L-amino acid) takes a right-handed helix form and gives minus b_0 in the Moffitt equation. Poly(R(+)-PO) and poly(R(+)-PS) consist of a repeating monomer unit of three atoms, just like poly(L-amino acid).†

Therefore, it is an interesting coincidence that poly(R(+)-PO) and poly(R(+)-PS) form a right-handed helix, not so rigid, of course, and that of poly(L-amino acid), and that the sign of Moffitt b_0 was also minus for both right-handed helices of poly(R(+)-PO) and poly(R(+)-PS). Theoretical treatment is being developed in our laboratory.

Table 1. ORD of Poly(R(+)-PO) and Poly(R(+)-PS)

	Poly(R(+)-PO)		Poly(R(+)-PS)	
	In CHCl_3	In benzene	In CHCl_3	In benzene
Sign of ORD	+	-	+	+
Proper equation for the ORD	Moffitt	Drude	Moffitt	Moffitt
Sign of Moffitt b_0	-		-	-

†Poly(L-amino acid) has an S-configuration around the asymmetric α -carbon atom, and the most stable conformation of S-amino acid residue in a poly(L-amino acid) results in a right-handed α -helix.

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