BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3663—3666 (1970)

The Effect of Solvents on the Optical Rotation of Poly(propylene Oxide)

Yoshiyuki KUMATA, JUNJI FURUKAWA and Takayuki FUENO*1

Department of Synthetic Chemistry, Kyoto University, Sakyo-ku, Kyoto

(Received March 28, 1970)

The change in the rotatory direction of optically active poly(propylene oxide) in different solvents has been discussed from the viewpoint of dielectric theory of solution. It has been pointed out that, in general, the shapes of the optical rotatory dispersion curves of polymers cannot directly be related to their conformation.

Price and Osgan[1] first noted that the optical rotation of poly(propylene oxide) measured at 589 mμ in chloroform and in benzene are of opposite sign. Tsunetsugu *et al.*[2] have suspected that this phenomenon might be due to a change in local polarizability of the asymmetric center effected by some weak complexation of polymer with solvent. Alternatively, Hirano *et al.*,[3] have interpreted this phenomenon as resulting from the formation of some helical component (gauche conformation) in chloroform solution.

According to the usual interpretation of optical rotatory dispersion, an optically active polymer having a helical conformation should exhibit an "anomalous" dispersion curve.[4] However, we have observed that the dispersion curves of poly(propylene oxide) prepared from optically active monomer are plain for all the solvents examined. In the present paper, we will reconsider the physical meaning of the anomalous dispersion, and show that the effect of solvents on the optical rotatory dispersion of poly(propylene oxide) might also be interpreted from a factor other than the conformational change of the polymer in different solvents.

Experimental

Optically active propylene oxide was polymerized by potassium hydroxide as a catalyst. The benzene solution of polymer was washed successively with dilute hydrochloric acid and water, and then freeze-dried. The molecular weight of the polymer obtained was determined by osmometry to be *ca.* 3200.

Measurements of the optical rotation of this polymer in various solvents were carried out at ambient temperature using a JASCO polarimeter Model ORD, UV-5. The concentration of polymer was fixed at 2.5 g/100 m*l*.

Results and Discussion

The specific rotation of poly(propylene oxide) at 589 mμ measured in various solvents is listed in Table 1. In any solvent used, the sample polymer gave a plain dispersion curve. Some typical curves are compared in Fig. 1, and the corresponding Moffitt-type plots (Eq. (1)) are shown in Fig. 2.

$$\frac{[M](\lambda^2-\lambda_0^2)}{\lambda_0^2} = a + \frac{b\lambda_0^2}{(\lambda^2-\lambda_0^2)} \qquad (1)$$

It may be seen in Fig. 2 that in all cases the values of $[M](\lambda^2-\lambda_0^2)/\lambda_0^2$ linearly decrease with increasing magnitudes of $\lambda_0^2/(\lambda^2-\lambda_0^2)$ and that no line crosses the zero line of $[M](\lambda^2-\lambda_0^2)/\lambda_0^2$ in the wavelength region of observation. This latter feature is in contrast to that encountered in the case of propylene oxide monomer, in which the quantity $[M](\lambda^2-\lambda_0^2)/\lambda_0^2$ becomes zero for some solvents (Fig. 3). In both Figs. 2 and 3, the values of λ_0 were chosen by the trial-and-error method so as to allow the best fit of observation to the Moffitt equation (1). The λ_0 values thus chosen are listed in Table 2.

It should be noted that the Moffitt equation (1) has proved to hold even in propylene oxide which has a rigid ring structure. Equation (1) was originally introduced as an approximation of Drude's two-term equation (2).[5]

$$[\alpha] = \frac{A}{\lambda^2-\lambda_1^2} - \frac{B}{\lambda^2-\lambda_2^2} \qquad (2)$$

The two-term equation of Drude has hitherto customarily been interpreted as equivalent to a summation of partial rotations originating from different

*1 Present address: Faculty of Engineering Science, Osaka University, Toyonaka, Osaka.

1) C. C. Price and M. Osgan, *J. Amer. Chem. Soc.*, **78**, 4787 (1956).

2) T. Tsunetsugu, J. Furukawa and T. Fueno, Preprint of 16th Symposium of Polymer Chemistry, Japan (1967), p. 402.

3) T. Hirano, S. Akutsu and T. Tsuruta, Preprint of 17th Symposium of Polymer Chemistry, Japan (1968), p. 1121; *J. Makromol. Sci.*, **A3**, 315 (1969).

4) M. Goodmann and M. Fried, *J. Amer. Chem. Soc.*, **89**, 1264 (1967).

5) J. Y. Cassim and E. Taylor, *Biophys. J.*, **5**, 553 (1965).

TABLE 1. OPTICAL ROTATIONS OF POLY(PROPYLENE OXIDE) IN VARIOUS SOLVENTS

Solvent	$[\alpha]_D$	$\frac{3[\alpha]_D}{n_D^2+2}$	Solvent	$[\alpha]_D$	$\frac{3[\alpha]_D}{n_D^2+2}$
A Benzene	−25.0	−17.6	R Tetrahydrofuran	+18.2	+13.7
B *N,N*-Dimethylaniline	−25.0	−16.9	S Ethylacetate	+13.6	+10.5
C Anisole	−25.5	−17.8	T *N,N*-Dimethylformamide	x	x
D Tetrachloroethylene	−9.3	−6.5	U Dimethylsulfoxide	x	x
E Carbon disulfide	−49.3	−31.8	V Cyclohexane	x	x
F Chlorobenzene	−24.0	−16.6	W Aniline	−15.4	−10.3
G Carbon tetrachloride	−7.4	−5.3	X Benzonitrile	−18.9	−13.1
H Hexamethylphosphoric triamide	+14.8	+10.8	Y Chloroform	+18.0	+13.2
I Pyridine	−19.8	−13.9	Z Acetone	x	x
J *p*-Dioxane	+9.6	+7.2	a Ethanol	x	x
K *o*-Nitroanisole	—	—	b Cyclohexanone	+15.3	+11.2
L Diethyl ether	x	x	d Methanol	x	x
M Triethylamine	x	x	e Acetonitrile	x	x
N Nitrobenzene	−18.8	−12.8	f 1,2-Dichloroethane	+4.8	+3.5
O Methylene iodide	—	—	g Methylene chloride	+6.0	+4.5
P *n*-Pentane	x	x	h Nitromethane	x	x
Q *N*-Methylacetamide	—	—	i Acetic acid	—	—
			j Water	x	x

——: Not determined.
x: Insoluble.

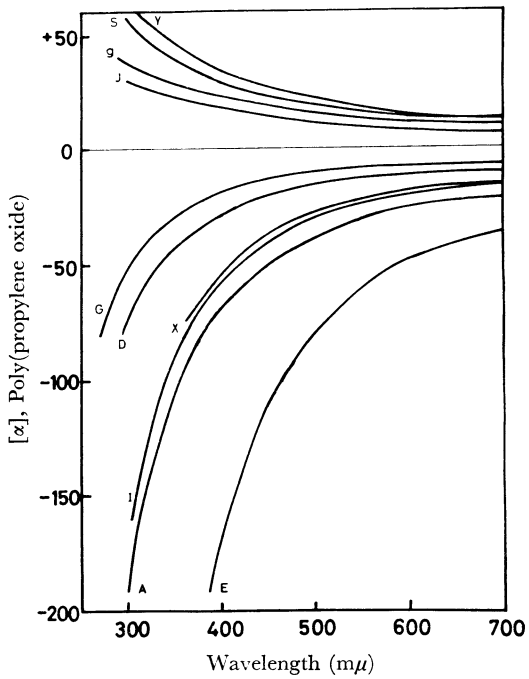

Fig. 1. The optical rotatory dispersion curves of poly(propylene oxide) in various solvents. The symbols appended to the curves indicate the solvents listed in Table 1.

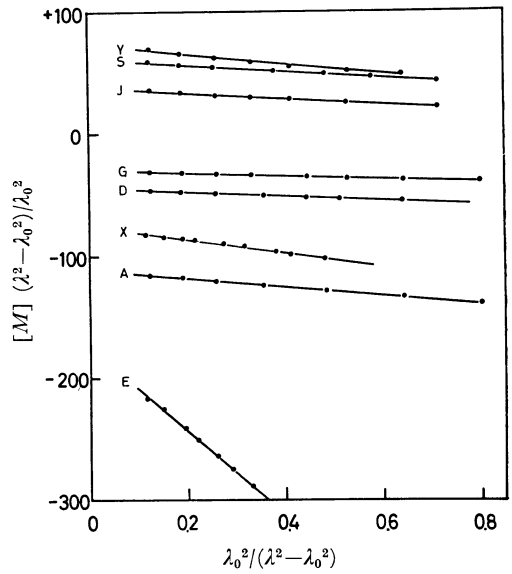

Fig. 2. Moffitt-type plots of the dispersion curves of Fig. 1. The symbols appended to the curves indicate the solvents listed in Table 1.

optical asymmetries of molecules. However, it is known that even the optical dispersions of several amino acids, which have only one asymmetric carbon, fit the two-term equation.[6] We thus feel it necessary to reconsider physical meanings underlying equations (1) and (2).

Let us briefly outline the fundamental logic necessary for understanding optical rotatory dis-

6) L. I. Katzin and E. Gulyas, *J. Amer. Chem. Soc.*, **86**, 1655 (1964).

Table 2. The best fitted λ_0 values for figs. 2 and 3

Solute		Solvent	λ_0 (mμ)
Poly(propylene oxide)	Y	Chloroform	150
	S	Ethyl acetate	200
	J	Dioxane	130
	G	Carbon tetrachloride	160
	D	Tetrachloroethylene	200
	X	Benzonitrile	230
	A	Benzene	210
	E	Carbon disulfide	150
Propylene oxide	A	Benzene	180
	J	Dioxane	160
	V	Cyclohexane	180
	d	Methanol	165
	j	Water	155

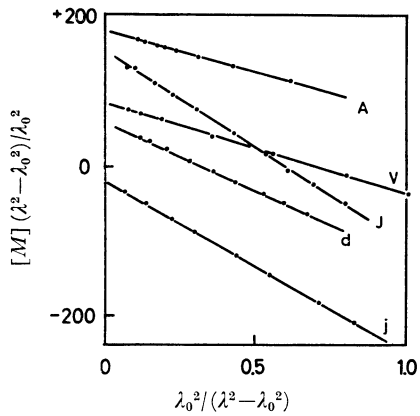

Fig. 3. Moffitt-type plots of optically active propylene oxide in various solvents. The symbols appended to the curves indicate the solvents listed in Table 1.

persion. Theoretical interpretation of the optical rotation owes much to Fresnel's equation

$$\alpha = \frac{\pi}{\lambda} x(n_R - n_L) \tag{3}$$

where α is the optical rotation expressed in the radian scale, x is the optical path length, and n_R and n_L are the refractive indexes of the right- and left-handed circular polarized lights, respectively. It is known that the refractive indexes themselves are subject to dispersion, as may be represented, for example, by the Ketteler-Helmholtz equation (4) or the Sellmeier equation (5).[7]

$$n^2 = a + \sum_m \frac{b_m}{\lambda^2 - \lambda_m^2} \tag{4}$$

$$n^2 = 1 + \sum_i \frac{A_i}{\lambda^2 - \lambda_i^2} \tag{5}$$

Quantum-mechanical treatments[8] of the refraction support the form of Eq. (4).

From Eqs. (3) and (5), coupled with suitable approximations, we may derive Drude's many-term equation[7]

$$[\alpha] = \sum_i \left(\frac{A_{iR}}{\lambda^2 - \lambda_{iR}^2} - \frac{A_{iL}}{\lambda^2 - \lambda_{iL}^2} \right) \tag{6}$$

In short, the optical rotatory dispersion can be interpreted as a difference in the refractive dispersions of the two polarized light beams. Hence, an "anomalous" dispersion that does not conform to Drude's one-term equation does not suggest that there exist more than one type of asymmetric center in the system under examination. This conclusion finds strong support in our previous demonstration that even monomeric R-propylene oxide, which has only asymmetric center, exhibits an anomalous dispersion.[9]

We now inquire why each term of Drude's equation should depend on solvent. According to the dielectric theory,[10] it is considered that, in a non-spherical cavity field which is surrounded by partially oriented solvent, both polarization and polarizability tensor of solute are transformed by change of solvent. This in turn will effect a change in the difference between the refractive indexes of the right- and left-handed circular polarized lights. The change will usually be very small but large enough to influence the optical rotation which may be calculated from equation (3). In the case of quartz,[7] for example, the difference in refractive indexes at 589 mμ is calculated from its optical

7) P. Drude, "The Theory of Optics," translated edition, Longmans Green and Co. (1920), Chapter 6.

8) J. H. Van Vleck, "The Theory of Electronic and Magnetic Susceptibilities," Oxford University Press, Oxford (1932), Chapter 8.

9) Y. Kumata, J. Furukawa and T. Fueno, This Bulletin, **43**, 3920 (1970).

10) a) K. Higashi, *Bull. Inst. Phys. Chem. Res.*, **14**, 146 (1935). b) H. Frölich, "Theory of Dielectrics," Oxford at the Clarendon Press (1949), Chapters 2 and 3.

rotation ($[\alpha]_D=2170°$) to be 0.000071, so that the variation in the refractive index difference by 0.00001 should lead to a variation in $[\alpha]_D$ amounting to *ca.* 310°. In some cases, the influence of solvent on polarization and polarizability of solute may become complicated to cause a change even in the direction of optical rotation.

It is difficult to express the shape of cavity and the degree of orientation by numeral parameters. Thus we will examine the effects of solvent on the optical rotation only qualitatively in terms of some empirical polarity parameter of solvents.

In Fig. 4 are shown the relations of the rotivities of propylene oxide and poly(propylene oxide) with the solubility parameter of solvents. Here, a rotivity is described by the equation[11]

$$\text{rotivity} = \frac{[\alpha]_D}{n_D^2+2} \qquad (7)$$

According to Herbandson *et al.*, the solubility parameter is a kind of polarity parameter of solvents.[12]

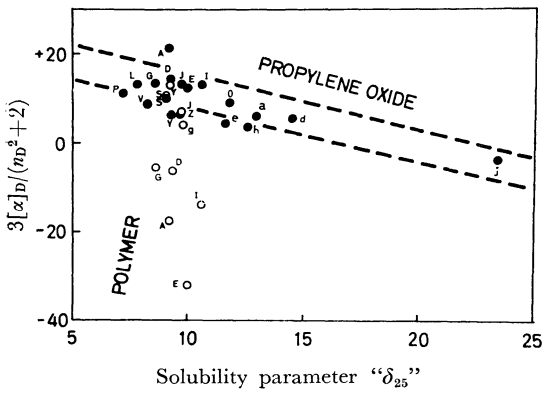

Fig. 4. Plots of the optical rotations of R-propylene oxide and its polymer measured in various solvents against the solubility parameter of the solvents. The symbols attached to the plots indicate the solvents listed in Table 1.

It may be seen in Fig. 4 that the rotivity of the monomer is dependent on the solubility parameter of solvents just in the same manner as it depended on various solvent polarity parameters.[9]

The rotivity of the polymer, on the other hand, appears not to be related with the solubility parameter in any simple manner. However, because the rotivities themselves of the monomer and polymer observed in various solvents are roughly correlated with each other as may be seen in Fig. 5. The polymer rotivity might increase with increasing solubility parameter of solvents, in contrast to the monomer rotivity.

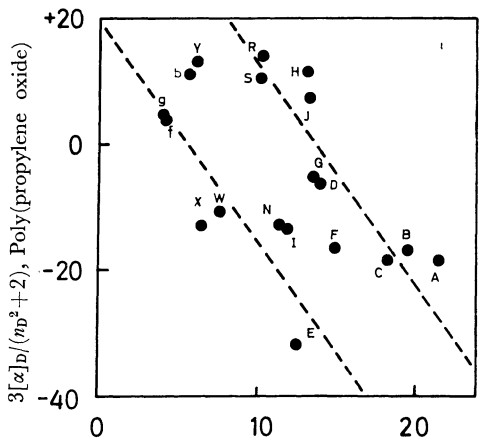

Fig. 5. The rotivity of polypropylene oxide *vs.* that of propylene oxide. The symbols attached to the plots indicate the solvents listed in Table 1.

In a solvent having a large solubility parameter, our polymer is hardly soluble and is aggregated. However, the variation of rotatory direction would not be due to the aggregated conformation, because even propylene oxide which has a rigid skeltal structure is apparently subject to variation in rotatory power in varying solvents. A similar situation is reported in isofenchon,[13] conformation of which is also difficult to change because of its rigid bicyclic ring structure.

Moreover, we found a poly(propylene oxide) film casted from the polymer melt to have a large negative rotation; the α_D value observed for a polymer film of 0.04 mm in thickness being $-1.5°$, a value which leads to a specific rotation of *ca.* $-2000°$. The specific rotation observed is far greater in magnitude than that reported by Hirano *et al.* for a film casted from solution. The different results are probably because our film was formed with polymer molecules highly oriented as in a liquid crystal.

In conclusion, the variation in the rotatory dispersion of poly(propylene oxide) with solvent can be interpreted, at least partially, as a result of the different variations of the refractive indexes toward the right- and left-handed circular polarized lights. The dispersions of the refractive indexes toward the two polarized light beams probably are influenced in a different way by the so-called cavity field which is induced by partially oriented polar solvents.

The authors are grateful to Mr. Ikuo Morino for assistance in the numerical analysis of the dispersion curves.

11) R. Gans, *Z. Phys.*, **27**, 164 (1924); *Ann. Phys. Leipzig*, (4), **79**, 547 (1926).

12) H. F. Herbrandson and F. R. Neufeld, *J. Org. Chem.*, **31**, 1140 (1966).

13) H. P. Gervais and A. Rassat, *Bull. Soc. Chim. Fr.*, **1961**, 743.