Far Infrared Spectra and Torsional Vibrations of Polyoxymethylene

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In the previous paper[1], it was reported that the results of the calculation of the normal vibrations of polyoxymethylene (POM) were in fairly good agreement with the observed infrared and Raman frequencies. In that case, the measurements were limited to the region higher than 300 cm^{-1}, and the torsional coordinates were neglected in the calculation. Although the infrared spectra of POM and POM-d$_2$ have been already measured in the region of 5000～300 cm^{-1} by Novak and Whalley[2], the spectra in the far infrared region have not yet been reported. In this communication, we will report the results of the far infrared measurements of POM and POM-d$_2$, and of the consideration about the torsional vibrations of the skeletal chain.

The spectra were measured by using a single beam far infrared spectrophotometer constructed in the Faculty of Engineering of this University. The detail of the spectrophotometer was described in the previous report[3]. A film sample of POM (3 cm. × 7 cm. × 0.03 mm.) was prepared from pellets of Delrin-acetal resin (du Pont Corporation) by rolling between a couple of heated rolls. The polarization spectra of POM were also measured by using a transmission polarizer made of polyethylene sheets[4]. The spectrum of POM-*d*$_2$ (paraformaldehyde-d$_2$ manufactured by Merck & Co., Inc.) was measured as Nujol paste.

The results are shown in Fig. 1. A parallel band (belonging to the A$_2$ species) was found at 235 cm^{-1} in the spectra of POM[5] and a band was found at a slightly lower frequency (212 cm^{-1}) in the spectrum of POM-d$_2$.

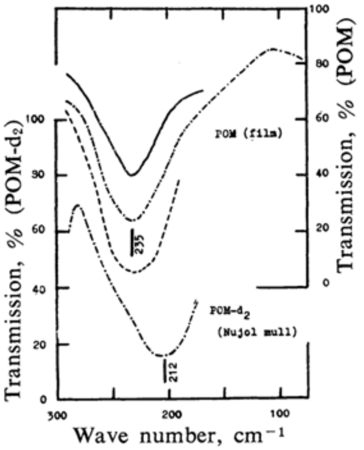

Fig. 1. Far infrared spectra of POM and POM-d$_2$.

-·-· Unpolarized
—— Electric vector perpendicular to the orientation direction
---- Electric vector parallel to the orientation direction.

The calculation of the normal vibrations was carried out by using the Urey-Bradley potential field according to the method described in the previous papers[6]. In this calculation the torsional displacement coordinates of the skeleton were taken into account. The numerical computation was made by using a NEAC 2203 electronic digital computer installed in the Computation Center of this University. The results show fairly good agreement between the observed and calculated frequencies. The maximum and average deviations are 6.15 and 2.19% for POM, and 9.90 and 2.51% for POM-d$_2$, respectively. The detailed results of the vibrational calculations will be reported in elsewhere.

As to the bands at near 200 cm^{-1}, the calculated frequencies [POM: 237 cm^{-1} (A$_2$), POM-d$_2$: 212 cm^{-1} (A$_2$)], are in good agreement with the observed results. The potential energy distributions calculated for the A$_2$ 235

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[1] H. Tadokoro et al., *J. Chem. Phys.*, **35**, 369 (1961).

[2] A. Novak and E. Whalley, *Trans. Faraday Soc.*, **55**, 1484 (1959).

[3] H. Yoshinaga et al., *J. Opt. Soc. Am.*, **48**, 315 (1958).

[4] A. Mitsuishi et al., ibid., **50**, 433 (1960).

[5] This frequency (235 cm^{-1}) agrees with the calculated values, 253 cm^{-1}, for the skeletal model of POM by Miyazawa (*J. Chem. Phys.*, 35, 693 (1961)).

[6] H. Tadokoro. *J. Chem. Phys.*, **33**, 1558 (1960); **35**, 1050 (1961).

and 212 cm^{-1} bands are $\tau_a(96\%)+r(CH_2)(3\%)$ and $\tau_a(93\%)+r(CD_2)(5\%)$, respectively⁷⁾. The E_1 fundamental of the lowest frequency (calculated as 22 cm^{-1} for POM and 21 cm^{-1} for POM-d$_2$) corresponds to the approximately pure torsional vibration of the skeleton with the potential energy distribution $\tau_s(56\%)-\tau_a(40\%)$ for both POM and POM-d$_2$⁷⁾. These bands could not be observed definitely because of the difficulties in the experimental technique in this region.

The torsional force constant F_τ was defined so that the diagonal elements of the $\boldsymbol{F}$-matrix associated with the torsional coordinates are expressed as $R_0^2 \sin^2 \Theta_0 F_\tau$, where R_0=equilibrium C–O distance and Θ_0=equilibrium COC or OCO angles. The value of F_τ was calculated to be 0.061 md/Å, from which the height of the potential barrier for the internal rotation about the C–O bond, V_0, can be estimated by using a sinusoidal potential function

$$V=(V_0/2)(1-\cos 3\phi)$$

where $\phi=\tau-\tau_0$. V_0 was found to be 3.6 kcal./mol.

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7) τ_a and τ_s denote the antisymmetric and symmetric combinations of two torsional coordinates for adjacent skeletal bonds, respectively.