

Short Communications

Dichroism and Depolarization of Vibration Spectra of Polyphenylene Oxides

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In connection with studies on the structure and properties of 2,6-disubstituted polyphenylene oxides it was found necessary to determine the orientation and anisotropy of unstressed and stressed polymers in the solid state.¹ Recent reviews on investigations of the vibration spectra of solid polymers indicate that these phenomena can conveniently be examined by measuring frequency shifts,² Raman spectroscopic dichroism effects^{3,4} or infrared spectroscopic dichroism.⁵ As a continuation of our previous spectroscopic work on polymers in the solid state⁶ we have examined the vibration spectra of stressed and unstressed poly-2,6-dimethyl-(1,4-phenylene oxide) (PPO) and poly-2,6-dimethoxy-(1,4-phenylene oxide) (PPOO) films.

Experimental. PPO was of commercial origin. PPOO was synthesized by polymerization of 2,6-dimethoxy phenol in the presence of silver oxide in triethylamine–chloroform.⁷ The viscosity average molecular weights \bar{M}_v obtained were 62 000 for PPO and 150 000 for PPOO.

From chloroform solutions (PPO–CHCl₃ = 1:7 and PPOO–CHCl₃ = 1:10 by weights) 60 μm thick films were drawn by a spiral roller on polytetrafluoroethylene plates. The moist films were detached and stretched by 40–60%, after which they were clamped in metal frames and carefully dried. The effect of mechanical stress on the vibrational spectra of these polymers was examined by dichroic ratios of infra-red absorption peaks and by laser Raman spectroscopy.

The infrared spectra were recorded with a grating spectrometer, model Perkin-Elmer 621. The dichroism was measured with an AgBr wire-grid polarizer. In the cell compartment the direction of

strain made an angle of 45° with the vertical. The plane of the polarizer was either in the direction of strain or perpendicular to it. With such a measuring method it was possible to work with a constant attenuation of the light beam and to compare directly the absorbances A_{\parallel} and A_{\perp} . All measurements were made at room temperature. The Raman spectroscopic studies were performed with a Jarrell-Ash 25–300 spectrometer. The 488.0 nm exciting line of an Ar–Kr laser (2 W) was used, with plasma filtering to protect the samples against heat. The samples were illuminated for several hours to reduce the fluorescence background, which interferes with the recording of the spectra.

The orientation process was also investigated with a polarizing microscope. In the unstretched films no polarizing effect could be observed, whereas in stretched ones a strong orientation was evident.

Results. The general feature and assignments of the infrared and Raman spectra together with the infrared dichroism and Raman spectroscopic depolarization ratios are given in Table 1.

The positions of the bands given are in good agreement with earlier infrared data.^{8,9} From the point of view of the present investigation, the bands associated with the chain motion, at about 1200 and 920–960 cm^{-1} , and with the substituents (–CH₃ and –OCH₃), at 1420–1490 and 1300–1380 cm^{-1} , are of special interest.

The bands at 1221, 1203, 925 and 845 cm^{-1} are shifted about 1–2 cm^{-1} toward lower frequencies when the PPOO films are stretched. Similar spectral trends have been observed by, among others, Evans and Hallam² in Raman spectra of polypropene, polycarbonate, polystyrene and nylon-6,6 on tensile-testing dumbbells and by Korsakov and co-workers¹⁰ in the infrared.

From Table 1 it is evident that, in contrast to the very small infrared spectral shifts on stretching the films, large changes in dichroism ratios are observed. Thus in PPO and PPOO no dichroism is noted in the unstretched state, whereas on stretching both σ -dichroism ($A_{\parallel}/A_{\perp} < 1$) and π -dichroism ($A_{\parallel}/A_{\perp} > 1$) up to 50% are observed for several of the infrared bands. Especially involved are the bands at 1605, 1492, 1446, 1417, 1126 and 991 cm^{-1} in PPOO. Similar trends are observed for the corresponding bands in PPO.

Table 1. Infrared and Raman spectroscopic data of poly-2,6-dimethyl-(phenylene oxide) (PPO) and poly-2,6-dimethoxy-(phenylene oxide) (PPOO).

Assignment	PPO				PPOO			
	IR (cm ⁻¹)	A /A _⊥	Raman (cm ⁻¹)	A /A _⊥	IR (cm ⁻¹)	A /A _⊥	Raman (cm ⁻¹)	A /A _⊥
ν CH	3020 w				3620 w 3460 w 3000 m 2965 m 2935 m	1.0	2950 w	0.86
ν_{as} ν_{as} CH ₃	2953 m					0.94		
ν_s $2\delta_{as}$ CH ₃	2922 m	1.0	2925 w	1.0				
ν_s CH ₃ $2\delta_s$ CH ₃	2850 w				2838 m	1.0	2842 w	1.10
ν C—C	2785 w							
δ_{as} CH ₃	1697 w				1605 s	1.06	1605 s	1.0
$\delta_{as} +$ CH ₃	1605 s	1.1	1605 w		1492 s	1.30		
$\delta_{as} +$ CH ₃	1470 s				1464 s	0.79		
$\delta_{as} +$ CH ₃	1438 m				1446 s	1.40		
(—OCH ₃)	1425 m				1417 s	0.90		
δ_s CH ₃	1380 m 1362 m	1.3	1380 w	1.10				
δ_s CH ₃								
CH ₃					1355 w			
CH ₃	1307 m		1308 w	0.82	1330 w	1.43	1334 m	0.89
ν_a (O ϕ) ^a	1190 s				1221 w	0.82	1215 w	0.90
	1142 w				1203 s	1.50		
ν_s OCH ₃					1126 s	0.90		
δ CH	1115 w	1.1						
OCH ₃					1105 m			
δ_{as-} CH ₃	1021 s	(2.0)			1035 m	1.08	1048 m	0.99
					991 s	1.33		
ν_s (O ϕ)	960 m	1.2	962 w	0.70				
γ CH	859 m	0.9			925 s	1.0	930 w	0.34
1,2,3,5-tetra(ϕ)	832 m	1.5	835 w	1.67	845 m	1.33	850 m	0.97
parasubst.(ϕ)	758 m				813 m	0.82		
arom. C=C	668 w				775 m			
1,2,3,5-tetra(ϕ)	595 w		575	0.95	665 w		604 w	1.10
	475 w				620 w			
					521 w			
							373	1.0
							77	0.86

^a ϕ = Phenyl.

It is generally a difficult task to get sufficiently strong depolarization effects in the Raman spectra of polymers, owing to internal interactions in the materials. The best results are presently obtained with thin films and polymer melts.¹¹ Oriented films, fibers and fiber bundles have also been tested.^{12,13}

In the present case only one real depolarized band was observed: namely, in connection with the ν_s

(ϕ -O- ϕ) vibration at 962 and 930 cm⁻¹ for PPO and PPOO, respectively. This effect indicates, however, the strong influence of the orientation of the material on the chain motion.

Discussion. The above effects have been interpreted in several ways. According to Evans and Hallam² and Cunningham and co-workers¹⁴ dichroism in IR spectra and changes in Raman spectra, e.g., in poly(ethylene terephthalate) may

be caused, on drawing, by changes in molecular conformations. Zhurkov, Korsukov and co-workers¹⁰ and Gubanov,¹⁵ on the other hand, favour an interpretation based on the stressing of the interatomic bands in the molecule.

It is difficult to decide between the two interpretations on the basis of the present data alone. Earlier thermodynamic work on PPO and PPOO by our group¹⁶ indicated that the increased volume of side chain groups in PPOO causes the glass transition to move to a lower temperature. This effect is attributable to both the flexibility of the side chain substituents and the decreased intermolecular effects. In the light of the above-mentioned results, the present dichroism and depolarization effects could be attributed partly to changes in intermolecular effects due to changes in free volume on orientation and partly to changes in valence angle motions of the main chain due to locking of the bulky side groups.

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1. Lindberg, J. J., Jauhiainen, T.-P. and Savolainen, A. *Pap. Puu.* 54 (1972) 91.
2. Evans, R. A. and Hallam, H. E. *Polymer* 17 (1976) 838.
3. Hendra, P. J. *Adv. Polymer Sci.* 6 (1969) 151.
4. Turrell, G. *Infrared and Raman Spectra of Crystals*, Academic, London—New York 1972.
5. Dechant, J. *Ultrarotspektroskopische Untersuchungen an Polymeren*, Akademie-Verlag, Berlin 1972.
6. Lindberg, J. J., Stenman, F. and Laipio, I. *J. Polymer Sci.*, Symposium No. 42 (1973) 925.
7. Jauhiainen, T.-P. and Lindberg, J. J. *TTA, Tutkimus ja Tekniikka* 2 (1975) 32.
8. Lindberg, J. J., Savolainen, A. and Starck, P. *Suom. Kemistil. B* 42 (1969) 120; Savolainen, A. *Thermodynamic and Relaxation Studies on 2,6-Disubstituted Polyphenylene Oxides*, Thesis, Helsinki 1974.
9. Hay, A. S. *J. Polymer Sci.* 58 (1962) 581.
10. Zhurkov, S. N., Vettergren, V. I., Korsukov, V. E. and Novak, I. I., *Proc. 2nd Int. Conf. Fracture*, Brighton (1969) 545; Korsukov, V. E. and Vettergren, V. I. *Strength Mater. (USSR)* 2 (1971) 51.
11. Vasko, P. D. and Koenig, J. L. *Macromolecules* 3 (1970) 597.
12. Snyder, R. G. *J. Mol. Spectrosc.* 36 (1970) 222.
13. Carter, V. B. *J. Mol. Spectrosc.* 34 (1970) 356.
14. Cunningham, A., Ward, I. M., Willis, H. A. and Zichy, V. *Polymer* 15 (1974) 749.
15. Gubanov, A. I. *Mekh. Polim.* 3 (1967) 771.
16. Savolainen, A. *Makromol. Chem.* 172 (1973) 213.

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