Polymer Bulletin 1, 61–66 (1978)

Polymer Bulletin

Polarized Raman Spectra of Doubly Oriented Poly(vinyl alcohol)

Kohji Tashiro, Masamichi Kobayashi and Hiroyuki Tadokoro*

Department of Polymer Science, Faculty of Science, Osaka University,
Toyonaka, Osaka, 560, Japan

Abstract

Polarized Raman spectra of doubly oriented samples of atactic poly(vinyl alcohol) have been measured. The great usefulness of such polarized spectra has been clarified for the vibrational analysis. The normal coordinate treatments of syndiotactic and isotactic poly(vinyl alcohol) chain models gave good agreement between the observed and calculated frequencies.

For single crystals of nonpolymeric compounds, polarized Raman spectra have widely been used in spectroscopic investigations. This technique should be also applied to the case of high polymeric substances. However, most of Raman spectral measurements done in the past were restricted to unoriented or uniaxially oriented samples of polymer materials. The detailed interpretation of spectra naturally requires the polymer specimens whose three crystal axes can be clearly distinguished from each other. HENDRA et al. (1977) measured a set of Raman spectra of different polarizability tensor components on a sample of single crystal texture polyethylene with approximate orientation in three senses. But there have been no reports about preparation of such large and single-crystal like polymer samples other than polyethylene so that they cannot be recognized as a general way of approach. Then we turned our attention to the doubly oriented samples of various crystalline polymers with three-dimensional orientation. In the present paper we choose atactic poly(vinyl alcohol) [at-PVA] as the first example (Figure 1). About twenty years ago, we measured the infrared spectra of doubly oriented at-PVA samples, the pleochroism of which led us to the definite assignment of the various important bands, for example, the 1141 cm^{-1} crystallization sensitive band (TADOKORO et al. 1958). The present paper will show that the polarized Raman spectra of doubly oriented samples of at-PVA are very useful to the interpretation of vibrational bands.

0170-0839/78/0001/0061/$01.20

Experimental

Doubly oriented samples of at-PVA were prepared according to the method previously described (TADOKORO et al. 1958). Degree of double orientation was checked by x-ray diffraction. For Raman measurements the rectangular specimens of 5 mm (draw direction) x 2 mm (width) x 0.3 mm (thickness) were cut out. Deuteration of the hydroxyl group of doubly oriented samples was performed in a small glass ampule (TADOKORO 1959), which was then used as a sealed Raman tube. Polarized Raman spectra were taken with a Japan Spectroscopic Company R750 triple monochrometer Raman spectrophotometer and 5145 Å line from an argon ion laser was used as an excitation source.

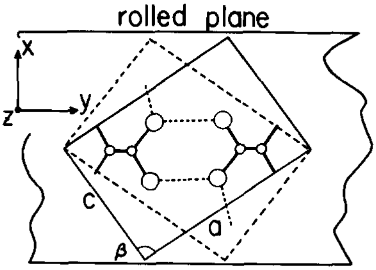

Figure 1. Relationship between the unit cell and doubly oriented sample of at-PVA

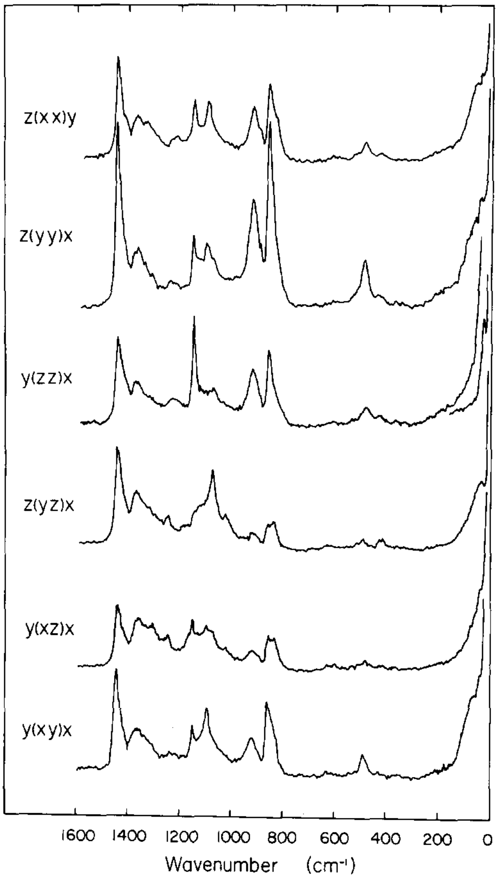

Figure 2. Polarized Raman spectra of doubly oriented at-PVA

Results and Discussion

The six different polarized Raman spectra of doubly oriented at-PVA in the frequency region below 1500 cm^{-1} are shown in Figure 2; the spectra of (xx), (yy), and (xy) polarizability tensor components and those of (yz) and (zx) components can be distinguished from each other, different than the case of uniaxially oriented specimens. Here, each component of polarizability tensor is represented using the so-called Porto's notation (DAMEN et al. 1966); the terms in parentheses indicate the measured tensor components based on the coordinate system defined in Figure 1.

Since the molecular plane is almost parallel to the rolled plane (TADOKORO et al. 1958), we can regard in a good approximation the coordinate axes fixed on the sample as those fixed on the molecular chain.

Vibrational analysis of Raman spectra and normal coordinate treatments for single chain have been carried out under the assumption of the spectra of at-PVA as simple overlapping of the spectra of syndiotactic and isotactic structures. If the hydroxyl group is approximated by one united atom, the factor group symmetry of st-PVA becomes isomorphous to the point group C_{2v} and that of it-PVA to C_s. The polarizability tensor components belonging to each symmetry species are given in Table I, where the infrared pleochroism is also indicated. The force constants used in the normal mode calculation will be reported soon with the results of vibrational analysis of the lattice modes. The calculated results are shown in Table II. [Shimanouchi (1964) presented the calculated results in comparison with the infrared spectra, which are essentially the same as those in Table II.]

Figure 3 shows the Raman spectra in the frequency region of 800 - 1300 cm^{-1}. As stated above, a group of bands with complicated profiles can be clearly separated from each other by the characteristic polarizations. The 1075 cm^{-1} band, for example, is the most intense in (yz) polarization and can be immediately assigned to the B_2 (anti-symmetric skeletal stretching) mode of st-chain (or A" of it-chain). The band 1100 cm^{-1} appears strongly in the (xy) component of spectra, being unambiguously assigned to the B_1 symmetry species [ν(CO)] of st-PVA (or A' of it-PVA). This is consistent with the infrared polarization perpendicular to both the rolled plane and the fiber axis, as shown in Tables I and II. The 1150 cm^{-1} band appears in the (zz) polarization. Figure 4 shows Raman spectral change on deuteration of the hydroxyl group. This band shifts to higher frequency side by about 10 cm^{-1}. Besides it intensifies with the increment of crystallinity of sample. These observations are consistent with the behavior of infrared band of 1141 cm^{-1}

TABLE I

Polarization Character of st- and it-PVA[a]

	Species	Polarizability	Transition Moment	
			to chain axis	to rolled plane
st-PVA	A_1	xx, yy, zz	⊥	//
(C_{2v})	A_2	zx	forbidden	forbidden
	B_1	xy	⊥	⊥
	B_2	yz	//	//
it-PVA	A'	xx, yy, zz, xy	⊥	⊥, //
(C_s)	A"	yz, zx	//	//

[a] The coordinate axes are referred to Figure 1.

(TADOKORO 1959) and therefore these infrared and Raman bands are considered to originate from the same normal mode. Infrared pleochroism of this band indicates that the transition moment is perpendicular to the draw direction and parallel to the rolled plane. By combining the polarization properties of infrared and Raman spectra with the calculated results of normal modes in Table II, this band can be definitely assigned to the totally symmetric skeletal stretching mode. The assignments of the bands thus made are summarized in Table II.

As understood from Tables I and II, polarization properties of most bands in infrared and Raman spectra can be explained in terms of the symmetry of st-PVA chain; i.e., we can say that the vibrational spectra of at-PVA can be approximated by those of st-PVA. This idea can be reasonable also from the viewpoint of mechanical property of the crystalline region (TASHIRO et al. 1978). But, of cource, we must not ignore some intense bands which cannot be ascribed to the st-structure. The band 860 cm^{-1} appears in the polarized Raman spectrum of the diagonal polarizability tensor component, not expected from the calculated results of normal modes of the st-chain in this frequency region. The infrared band corresponding to this Raman band has been said to be due to the it-part from the tacticity dependence (MURAHASHI et al. 1966). Infrared polarization and normal coordinate treatment are also consistent with this assignment (Tables

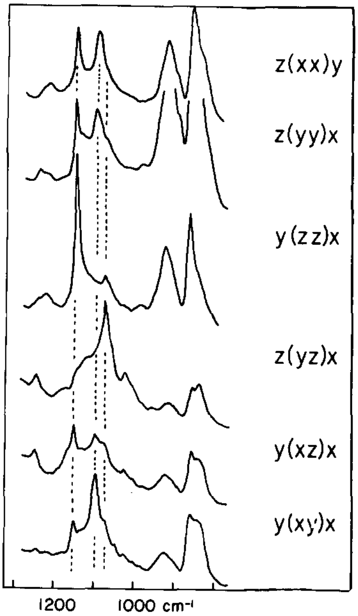

Figure 3. Polarized Raman spectra of doubly oriented at-PVA in 800 - 1300 cm^{-1}

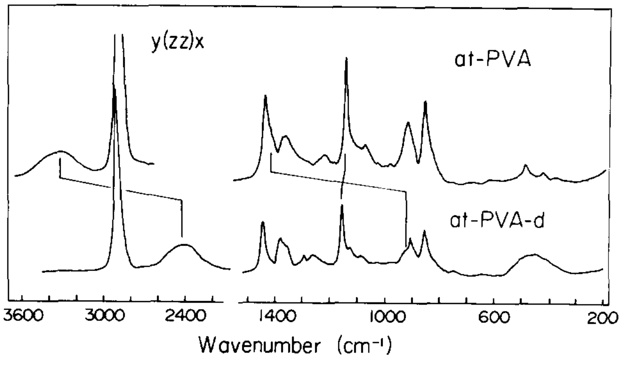

Figure 4. Raman spectral change on deuteration of OH group; (zz) component

TABLE II

Vibrational Assignments of at-PVA

Raman (cm^{-1})	IR (cm^{-1})^a	Calculated Values st-PVA	 it-PVA	Assignments
3300 [diag]^b	3340	-	-	ν(OH)
2950 [xy]	2942 [⊥,⊥]	2958 [B_1]	2961 [A']	$\nu_{as}(CH_2)$
2915 [diag]	2910 [⊥,∥]	2901 [A_1]	2902 [A']	ν(CH)
2845 [diag]	2840 [⊥]	2839 [A_1]	2838 [A']	$\nu_s(CH_2)$
1447 [diag]	1450 [sh]	1447 [A_1]	-	$\delta(CH_2)$
-	1440 [∥]	-	-	δ(OH)
1425 [?]	1420 [⊥]	1423 [A_2]	1425 [A']	$\delta(CH_2)$
1375 [n.p.]	1376 [?]	-	-	amorphous ?
1340 [diag]	1326 [⊥]	1344 [A_1]	-	δ(CH) + δ(CO)
1315 [yz?]	1315 [∥]	1319 [B_2]	1339 [A"]	w(CH_2) + w(CH)
1300 [zx?]	-	1299 [A_2]		w(CH)
1250 [yz]	1232 [∥]	1254 [B_2]	1249 [A"]	w(CH_2) + w(CH)
1225 [diag]	1215 [⊥]	1219 [A_1]	-	t(CH_2)
1150 [zz]	1141 [⊥,∥]	1150 [A_1]	1166 [A']	ν_s(CC)
-	-	-	1146 [A"]	t(CH_2)
1125 [?]	1125 [∥?]	-	-	amorphous ?
1100 [xy]	1093 [⊥,⊥]	1092 [B_1]	1082 [A']?	ν(CO)
1075 [yz]	1083 [∥,∥?]	1083 [B_2]	1106 [A"]	ν_{as}(CC)
1025 [?]	1040 [⊥,⊥]	-	1082 [A']?	ν(CO)?
980 [?]	-	-	-	?
922 [diag]	913 [⊥,∥]	926 [A_1]	-	ν(CO)
900 [?]	890 [⊥]	-	-	?
860 [diag]	849 [⊥,∥]	-	901 [A']	r(CH_2) + ν(CO)
835 [xy]	835 [⊥,∥]	831 [B_2]	-	r(CH_2)
630 [yz]	640 [∥]	-	-	o.p. OH
610 [zx]	610 [?]	622 [A_2]	-	θ(CCC)
525 [?]	525 [?]	499 [B_1]	-	θ(CCC)
485 [diag]	480 [⊥]	527 [A_1]	534 [A']	δ(CO)
430 [yz]	420 [∥]	402 [B_2]	379 [A"]	w(CO)
365 [diag]	375 [⊥]	-	353 [A']	τ(CC)
200 [diag]	200 [⊥]	135 [A_1]	-	τ(CC)
-	169 [∥]	123 [B_2]	-	τ(CC)

a. TADOKORO et al. 1958. b. [ ] indicates the polarizability for Raman and for IR (to fiber axis and to the rolled plane).

I and II). In the far-infrared spectra there appears an it-band at 375 cm^{-1} (calculated frequency 353 cm^{-1}).

About the Usefulness of Polarized Raman Spectra of Doubly Oriented Polymer Samples in the Vibrational Analysis

In the previous studies, we have demonstrated that the infrared pleochroism of doubly oriented samples of at-PVA and poly(ethylene terephthalate) gives a very useful information on the interpretation of vibrational spectra (TADOKORO et al. 1962). But in those cases we sliced a doubly oriented sample in the cross section perpendicular to the draw direction and the very small specimen thus obtained was set on an infrared microspectrometer; these operations were very difficult. Besides we could not measure the spectra over the wide frequency region. In the present study we have been able to exceedingly easily obtain much more valuable data of vibrational bands by the measurements of polarized Raman spectra using doubly oriented samples in a bulk form. The degree of three-dimensional orientation of polymer materials is not so high as that of single crystals. But even these polymer specimens show remarkably definite polarization, as revealed above for the case of at-PVA. Therefore they can offer us useful information for the vibrational analysis compared with the cases of unoriented and uni-axially oriented specimens. Such a device will be one of the much powerful methods for the structural study of crystalline polymers.

References

DAMEN, T. C., S. P. S. Porto, and S. B. Tell, Phys. Rev., 142, 570 (1966).
HENDRA, P. J., H. P. Jobic, and E. P. Marsden, Spectrochim. Acta, 33a, 445 (1977).
MURAHASHI, S., S. Nozakura, M. Sumi, and K. Matsuura, J. Polym. Sci., B, 4, 59 (1966).
TADOKORO, H., S. Seki, I. Nitta, and R. Yamadera, J. Polym. Sci., 28, 244 (1958).
TADOKORO, H., Bull. Chem. Soc. Jpn., 32, 1252 (1959).
TADOKORO, H., K. Tatsuka, and S. Murahashi, J. Polym. Sci., 59, 413 (1962).
TASHIRO, K., M. Kobayashi, and H. Tadokoro, to be published.
SHIMANOUCHI, T., J. Polym. Sci., Part C, 7, 85 (1964).

Received June 3, 1978.