

# High-pressure Raman studies of ultra-high-molecular-weight polyethylene

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This paper reports the Raman spectra of ultra-high-molecular-weight polyethylene (UHMWPE) at room temperature and under high pressure employing a Mao–Bell type of miniature diamond–sapphire anvil cell. Davydov splitting near  $1065\text{ cm}^{-1}$  and resonance interactions in the bending ( $1440\text{--}1470\text{ cm}^{-1}$ ) and C–H stretching ( $2840\text{--}2950\text{ cm}^{-1}$ ) regions of the Raman spectra of UHMWPE at high pressure are described. The dependences of mode Grüneisen parameters ( $r_i$ ) on vibrational frequency ( $\nu_i$ ) were determined at several pressures from the Raman spectra and compression experiments of UHMWPE.

(Keywords: ultra-high-molecular-weight polyethylene; Raman spectra; high pressure; Fermi resonance; Davydov splitting)

## INTRODUCTION

Although considerable effort has been devoted to the study of vibrational spectra of polymers<sup>1,2</sup>, only scant attention has been directed to the effect of pressure on the spectra. From Raman spectra of polymers, we can obtain a lot of information about the effects of pressure on polymers, such as the thickness of the crystal, structural change of the amorphous region, or the coupling between the different vibrational modes of crystalline and amorphous segments. The studies of vibrational spectra of polymers as a function of pressure are significant for the studies of the relationship between the structure and properties of polymers under high pressure. Wu and Nicol<sup>3</sup> have studied Fermi resonance in the vibrational spectra of polyethylene (PE) under high pressure; Wu *et al.*<sup>4</sup> have discussed the Grüneisen parameters of crystalline PE. This paper reports observations of the Raman spectra of ultra-high-molecular-weight polyethylene (UHMWPE) at room temperature and at high pressure by use of a diamond–sapphire anvil cell.

## EXPERIMENTAL

### Raman scattering

Hydrostatic pressure in the range of 0–2.5 GPa was applied on the bulk of UHMWPE sample at room temperature by a Mao–Bell type<sup>5</sup> of miniature diamond–sapphire anvil cell with 16:3:1 methanol–ethanol–water mixture for the hydrostatic pressure medium. The pressure was calibrated with the well known ruby fluorescence scale<sup>6</sup>. The back-scattering Raman spectra at each pressure were recorded by a Spex 1403 double-grating monochromator with a DMIB Datamate. The 5145 Å radiation from an argon-ion laser was used for excitation at an output power of 150 mW.

### Volume compression

The isothermal compression experiments on UHMWPE were carried out at room temperature in an end-loaded piston–cylinder high-pressure apparatus by monitoring piston displacements. Details of the experimental technique can be found elsewhere<sup>7</sup>. A specimen of appropriate length of UHMWPE was obtained by recrystallizing in vacuum. Machined cylindrical specimens slightly less than 11 mm diameter and 16 mm length were sheathed in indium. The cylinder obtained was used for the compressibility measurements.

## RESULTS AND DISCUSSION

### Raman scattering

Raman scattering group theory predicts eight allowed Raman-active modes for single-chain optical modes of PE<sup>8</sup>:

$$\Gamma_R = 3A_g + 2B_{1g} + 2B_{2g} + B_{3g} \quad (1)$$

In fact, a total of 11 peaks were observed in spectra of UHMWPE at atmospheric pressure (*Figure 1*), which agrees well with spectra reported from earlier studies<sup>9</sup>. The assignments of the fundamentals of PE chain and crystal are collected in *Table 1*. Spectra of UHMWPE at several pressures are shown in *Figure 2*, and pressure dependences of the Raman frequencies are plotted in *Figure 3*. It can be seen that the band shift at  $1170\text{ cm}^{-1}$  is nearly pressure-independent and the band shift at  $1417\text{ cm}^{-1}$  decreases with increasing pressure. These indicate that  $\text{CH}_2$  rocking vibration at  $1170\text{ cm}^{-1}$  does not change and  $\text{CH}_2$  bending vibration at  $1416\text{ cm}^{-1}$  tends to weaken on increasing the pressure. The normal behaviour is for Raman frequency to increase appreciably with increasing pressure. All other Raman frequencies of UHMWPE in the range of  $1000$  to  $2900\text{ cm}^{-1}$  do increase with pressure, but perhaps most importantly there are great changes in the neighbourhood of the  $1065\text{ cm}^{-1}$

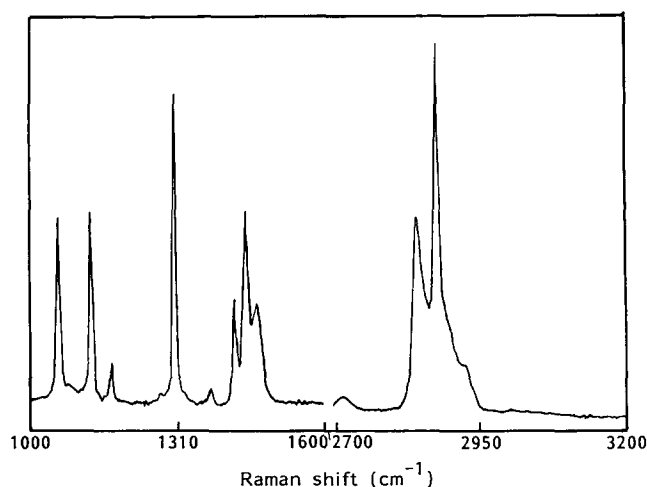
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**Table 1** Assignment of the fundamentals of the polyethylene chain and crystal

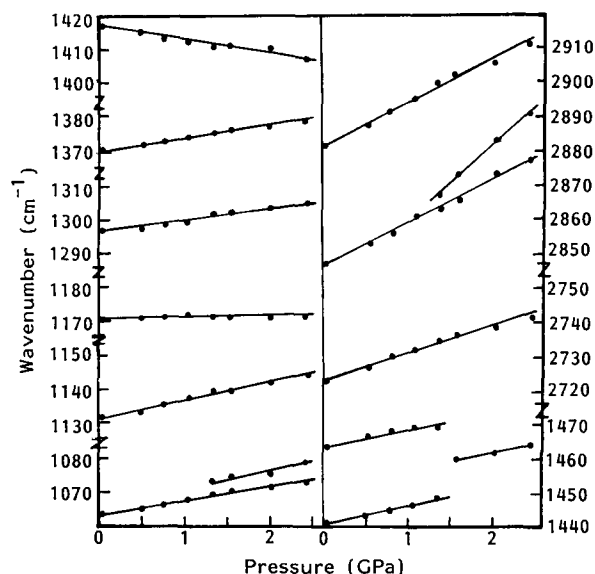
Isolated-chain species <sup>a</sup>	Crystal species <sup>b</sup>	$\nu$ (cm <sup>-1</sup> )		Description
		Ref. 9	This work	
$b_{1g(xy)}$	$A_g$	2880	2887	Asymmetric CH stretch
	$B_{3g(xy)}$			
$a_g$	$A_g$	2845	2849	Symmetric CH stretch
	$B_{3g(xy)}$			
$a_g$	$A_g$	1416	1417	CH <sub>2</sub> bend (scissors)
	$B_{3g(xy)}$ }	1466	1463	
		1442	1441	
$b_{2g(zx)}$	$B_{1g(yz)}$	1368	1370	CH <sub>2</sub> wa <sub>g</sub>
	$B_{2g(zx)}$	1373		
$b_{3g(xy)}$	$B_{1g(yz)}$	1296	1297	CH <sub>2</sub> twist
	$B_{2g(zx)}$	1294		
$b_{1g(xy)}$	$A_g$	1171	1170	CH <sub>2</sub> rock
	$B_{3g(xy)}$			
$a_g$	$A_g$	1132	1131	Symmetric CC stretch
	$B_{3g(xy)}$			
$b_{2g(zx)}$	$B_{1g(yz)}$	1063	1063	Asymmetric CC stretch
	$B_{2g(zx)}$	1065		

<sup>a</sup> The x and z axes are in the plane defined by the carbon skeleton; x is the parallel to the chain direction

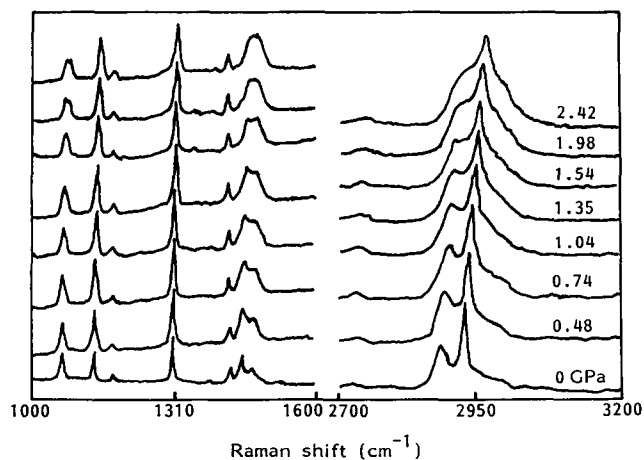
<sup>b</sup> The x and y axes are parallel respectively to the a and b axes of the crystal



**Figure 1** Raman spectra of UHMWPE at room temperature and atmospheric pressure



**Figure 3** The dependence of Raman shifts of UHMWPE on pressure



**Figure 2** Raman spectra of UHMWPE at several pressures

band and in the bending CH<sub>2</sub> region (1400–1470 cm<sup>-1</sup>) and C–H stretching region (2840–2950 cm<sup>-1</sup>), as shown in Figure 2. At 1.54 GPa a new peak appears at 1075 cm<sup>-1</sup>, but for intermediate-molecular-weight polyethylene a new peak appears below 1.20 GPa<sup>3</sup>. The changes of C–C stretching band B<sub>1g</sub> near 1065 cm<sup>-1</sup> are due to pressure-induced intermolecular Davydov splitting. The intermolecular forces responsible for the splitting have their origin in repulsion between non-bonded hydrogens. This phenomenon indicates that the effect of pressure on intermediate-molecular-weight polyethylene is stronger than on UHMWPE, since the latter has a more dense packing in view of structure. In the bending region of CH<sub>2</sub>, the intensity of the 1416 cm<sup>-1</sup> band apparently increases with increasing pressure; and in the C–H stretching region, the intensity of the

2849 cm<sup>-1</sup> band distinctly diminishes and the width of the 2887 cm<sup>-1</sup> band rapidly broadens with increasing pressure. The changes mentioned above are caused by pressure-induced Fermi resonance interaction<sup>3</sup>. Generally, provided that the frequencies of fundamental and binary combination are sufficiently close, and that certain symmetry requirements are met, the interaction of the localized mode with a binary combination (two-phonon state) that itself is conformationally dependent is called the Fermi resonance interaction. As a result, there is a frequency displacement of the two states that increases their separation; the binary state increases its intensity at the expense of the fundamental Fermi resonance interaction changes with pressure, as a general rule<sup>10</sup>. So the above changes are explained as follows. The increasing intensity of the 1464 cm<sup>-1</sup> band with pressure is attributed to change of the symmetry-allowed Fermi resonance interaction between the two crystalline factor group components A<sub>1g</sub> and B<sub>1g</sub> of the CH<sub>2</sub> bending fundamental and the three overtones (A<sub>1g</sub>) and combination (B<sub>1g</sub>) of the components of the infra-red-active CH<sub>2</sub> rock (B<sub>2u</sub> 720 cm<sup>-1</sup>, B<sub>3u</sub> 731 cm<sup>-1</sup>)<sup>3,11</sup>. The apparent diminution of the intensity of CH stretching fundamental and the broadening of CH asymmetric stretching fundamental are readily interpreted in terms of the symmetry-allowed resonance interaction between symmetric CH stretching fundamental and the appropriate binary combinations of CH<sub>2</sub> bending fundamental<sup>12</sup>. External pressure can perturb the energy states of a polymer, and thus cause bands of various intramolecular modes to shift. The frequencies of different intramolecular modes are generally expected to change by different amounts with the perturbation of pressure. The pressure dependences of their energies differ for the various normal modes, and thus pressure will perturb the extent of mixing of the vibrations and lead to Fermi resonance, and the symmetry of the molecule may be improved. We also find that the Raman spectra taken after the release of pressure and those before the pressure measurement are essentially the same. This indicates that no irreversible change of the crystal structure due to pressure occurs up to 2.5 GPa at room temperature.

#### Volume compression

The measured values of  $\Delta V/V_0$  by using the piston-cylinder apparatus are given in Table 2. The pressure dependence of  $\Delta V/V_0 (=1 - V/V_0)$  is represented by the expression:

$$1 - V/V_0 = aP + bP^2 + cP^3 \quad (2)$$

where  $a=0.1588$ ,  $b=-6.953 \times 10^{-2}$ ,  $c=1.276 \times 10^{-2}$  and  $P$  is in GPa. Using this equation, we can calculate

the Grüneisen constant<sup>13</sup>:

$$r = -b/a^2 - 2/3 \cong 2.193 \quad (3)$$

Here  $r$  is the macroscopic Grüneisen constant defined as the average value of mode Grüneisen parameters over all modes:

$$r_{(T)} = \sum c_i r_i / \sum c_i \quad (4)$$

where  $c_i$  are weighing factors. At a given temperature for any system there is only a single value for  $r$ ; however, its precise value cannot be calculated due to lack of information about all contributing modes. We also obtain bulk modulus  $B_0$  and first-order pressure derivatives  $B'_0$  of  $B_0$ <sup>14</sup>:

$$B_0 = 1/a = 6.4185, \quad B'_0 = -2b/a^2 - 2/3 = 4.7288$$

By expanding  $B_{(P)}$  in a Maclaurin series, we have approximately  $B_{(P)} = B_0 + B'_0 P$ ; thus compressibility is given by:

$$\begin{aligned} \beta &= 1/B_{(P)} = 1/(B_0 + B'_0 P) \\ &= 1/(6.4185 + 4.7288P) \end{aligned} \quad (5)$$

#### Grüneisen parameters of UHMWPE

The study of vibrational spectra as a function of pressure may reveal the intermolecular potential. The frequency shift with volume defines the so-called mode Grüneisen parameter. The mode Grüneisen parameters  $r_i$  are calculated using the formula:

$$r_i = -\frac{d \ln v_i}{d \ln V} = \frac{1}{\beta} \frac{dv_i}{v_i dP} \quad (6)$$

where the compressibility  $\beta$  is determined by equation (5). These calculated mode Grüneisen parameters of UHMWPE in the pressure range of 0–2.5 GPa are listed in Table 2. Since it is closely related to the intermolecular potential, the Grüneisen parameter is a useful parameter in the theoretical derivation of the equation of state for all substances. An understanding of  $r_i$  would provide insight into the nature of the polymeric solid state. It is readily seen from Table 2 that the Grüneisen parameters  $r_i$  of Raman-active modes are not monotonic decreasing functions of  $v_i$ . The theoretical prediction of  $r_i$  proposed by Broadhurst and Mopsik<sup>15</sup> can be rewritten as:

$$r_i v_i^2 / r_j v_j^2 = 1 \quad (7)$$

By comparing our data with equation (7), we find that the agreement is usually poor. The disagreement of equation (7) with the observed  $r_i$  is clearly due to the fact

**Table 2** Mode Grüneisen parameters of UHMWPE at high pressure (at 298 K)

$v_i(0)$ (cm <sup>-1</sup> )	$dv_i/dP$ (cm <sup>-1</sup> GPa <sup>-1</sup> )	$P$ (GPa) 0	$r_i$ ( $\times 10^2$ )									
			0.25	0.50	0.75	1.00	1.25	1.5	1.75	2.00	2.25	2.50
		$-\Delta V/V_0$ 0	0.0379	0.0645	0.0832	0.0973	0.1083	0.1196	0.1293	0.1378	0.1456	0.1526
1131	5.5557	3.1529	3.7290	4.3038	4.8771	5.4490	6.0195	6.5887	7.1564	7.7228	8.2878	8.8514
1170	0.6324	0.3470	0.4108	0.4746	0.5384	0.6022	0.6660	0.7298	0.7935	0.8572	0.9209	0.9846
1297	3.9330	1.9463	2.3031	2.6593	3.0149	3.3700	3.7246	4.0787	4.4322	4.7852	5.1377	5.4896
1370	3.3440	1.5668	1.8541	2.1412	2.4279	2.7143	3.0003	3.2860	3.5713	3.8563	4.1410	4.4253
1417	-3.2620	-1.4776	-1.7507	-2.0242	-2.2980	-2.5721	-2.8465	-3.1212	-3.3963	-3.6716	-3.9473	-4.2233
2723	7.7490	1.8266	2.1614	2.4959	2.8298	3.1632	3.4962	3.8288	4.1608	4.4924	4.8235	5.1541
2883	11.721	2.6095	3.0870	3.5635	4.0391	4.5136	4.9873	5.4600	5.9317	6.4025	6.8723	7.3411

that the contribution of the static crystalline potential to the normal modes is different for various normal modes.

## CONCLUSIONS

The splitting of C–C stretching band near  $1065\text{ cm}^{-1}$  was due to pressure-induced intermolecular Davydov splitting. The increasing intensity of  $1464\text{ cm}^{-1}$  band with pressure is attributed to change of the symmetry-allowed Fermi resonance interaction between the two crystalline factor group components  $A_{1g}$  and  $B_{1g}$  of the  $\text{CH}_2$  bending fundamental and the three overtones ( $A_{1g}$ ) and combination ( $B_{1g}$ ) of the components of the infra-red-active  $\text{CH}_2$  rock ( $B_{2u}$   $720\text{ cm}^{-1}$ ,  $B_{3u}$   $731\text{ cm}^{-1}$ ). The apparent diminution of the intensity of CH stretching fundamental and the broadening of CH asymmetric stretching fundamental are readily interpreted in terms of the symmetry-allowed resonance interaction between symmetric CH stretching fundamental and appropriate binary combinations of  $\text{CH}_2$  bending fundamental. The dependence of mode Grüneisen parameters ( $r_i$ ) on vibrational frequency ( $\nu_i$ ) was determined at several pressures from the Raman spectra and compression experiments on UHMWPE.

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