Longitudinal acoustic vibrations in polyethers and polythioethers

P. J. Hendra and H. A. Majid
Department of Chemistry, The University, Southampton SO9 5NH, UK

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A search has been made for polymers which exhibit in their Raman spectra bands originating in longitudinal acoustic vibrations. Features have been found in a range of poly(alkylene ethers) and polythioethers. It appears that if relatively extended runs of $CH_2—CH_2$ units separate the chalcogenide atoms, the polymers vibrate similarly to polyethylene. Hence, the Raman method can be used in identifying and estimating the thickness of lamellae in these cases.

INTRODUCTION

A number of well-established and valuable methods exist for the study of lamellar morphology in crystalline polymers, e.g. electron microscopy and low-angle X-ray diffraction (LAXD). All the available methods have their problems but have improved in their versatility and accuracy with time. Recently, a new experimental method has become available: the use of Raman spectroscopy to measure the frequency of the longitudinal acoustic vibration in lamellar species and hence to deduce their thickness. The method is attractive because it can be applied easily to large or small samples under wide ranges of temperature and pressure (see ref 1 and others cited therein). Unfortunately, the Raman method appears to be relevant to only a few polymers of which, currently, linear polyethylene is by far the most important. Applications to the study of polymer morphology are available[2,9].

Since the method is now of proven value, the search is on to discover more polymers where the longitudinal acoustic mode frequency can be measured and interpreted.

In this paper, we report the outcome of such a search.

EXPERIMENTAL

The materials whose Raman spectra were investigated had general formulae $\{(CH_2)_m - X\}_n$ where X = O or S and $m = 1–10$. Where possible, the samples were acquired from beneficiaries and commercial establishments as follows: Suga (X = O, m = 3); Machon, Etienne, Poulet and Boileau (X = S, m = 3); Russel and Fraser (X = O, m = 4); Du Pont Co., UK and Merck, Sharp and Dohme, Canada (X = O, m = 1); British Drug Houses (X = O, m = 2).

Samples with formulae X = O, m = 6 and 10 were prepared by polycondensation of the appropriate glycol in acidic media while those of formulae X = S, m = 4, 5, 6 and 10 were synthesized according to the reaction:

$$Na_2[S(CH_2)_mS] + Br(CH_2)_mBr \rightarrow \{(CH_2)_m - S\}_n + NaBr$$

The identity of each specimen was confirmed by microanalysis. Full details of the preparation methods used will be found in ref 3.

Raman spectra were recorded on a Cary 82 spectrometer fitted with an Ar^+ laser operating at 514.5 nm. This instrument uses a triple monochromator, thus allowing us to approach the exciting line closely. Melting points and other thermal data were obtained with a Perkin–Elmer D.S.C.-2 Calorimeter and density measurements were made by flotation.

Longitudinal acoustic modes

The vibrational characteristics of a polymer consist of three main types of vibrational modes: *internal modes* or the contortions of the polymeric molecule within itself considered as if it were in isolation; *lattice modes* which are gyrations of a molecule as a whole with respect to its neighbours in the crystalline lattice; and *acoustic modes*. The longitudinal type of acoustic mode, with which we are concerned here, can be described as an accordion-type deformation of the extended polymer backbone. In crystalline polymers, the main occurrence of extended backbones is in the cores of lamellae. Further, the simple principles of vibrating rods leads us to expect that the *LA* mode frequency will vary inversely with this core thickness[4]. The frequency ranges for the three types of motion are: *internal modes* ~3500–100 cm^{-1}; *lattice modes* ~250–20 cm^{-1}; *longitudinal acoustic LA modes* below 30 cm^{-1} in polymers.

The appearance of any mode as a band in the Raman scattering spectra or in infra-red absorption is governed by symmetry. As a consequence, the *LA* mode appears solely in the Raman spectrum and then only its 'odd' orders. Thus, to find bands due to this motion we need to study the Raman spectrum of a crystalline polymer between $\Delta\upsilon$ 100 cm^{-1} and the exciting line. Further, we must be able to discriminate between bands due to acoustic and lattice motions. Symmetry considerations and comparison with the low frequency infra-red spectrum can be helpful in this respect. Sometimes, however, the crystal structure of the polymer may not be reliably known and the far infra-red spectrum is determinable only with difficulty and on uncomfortably large specimens. Fortunately, there are means of unravelling this problem solely within the Raman effect since it has been observed that *LA* mode frequencies are relatively temperature-insensitive (unless there is a change in structure with temperature). On the other hand, lattice mode frequencies rise as the temperature of the sample is reduced. The latter comes about because the contraction of the molecular matrix at low temperature increases the intensity of the intermolecular force field.

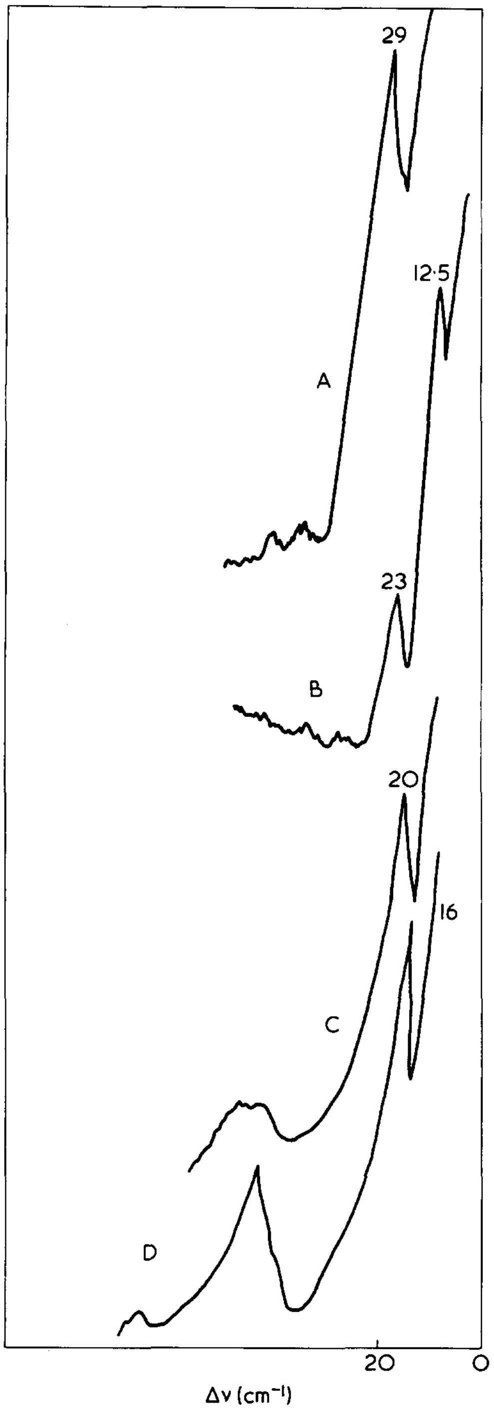

Figure 1 Low frequency Raman spectra of some poly(alkyl oxides) and poly(alkyl sulphides). A, $\{(CH_2)_{10} - O\}$, quenched melt; B, $\{(CH_2)_{10} - O\}$, annealed 75°C; C, $\{(CH_2)_{10} - S\}$, quenched melt; D, $\{(CH_2)_{10} - S\}$, annealed 85°C

When heat-treated just below their melting points, crystalline polymers with few exceptions increase in lamellar thickness. Thus, annealed samples are expected to show *shifted LA* mode frequencies but *similar* internal and lattice mode characteristics. The increase in lamellar thickness on annealing should also be accompanied by a corresponding increase in melting point and density.

RESULTS

In *Figure 1* we show some typical low frequency Raman spectra, while in *Table 1* we collect detailed data on a range of polyethers and polythioethers in melt-crystallized, solution-crystallized and annealed form. The densities and melting points have been observed to increase on annealing in all cases.

It is clear that after applying the tests described above, *LA* modes can be identified in cases: $\{(CH_2)_m - O\}_n$ m = 4, 6 and 10 and $\{(CH_2)_m - S\}_n$ m = 3, 4, 5, 6 and 10. Checks on the polyethers where $m < 4$ indicate no appearance of *LA* mode characteristics. On the other hand, poly (ethylene sulphide)[5] $\{(CH_2)_2 - S\}_n$ shows superb spectral features due to acoustic motions but poly(methylene sulphide) $\{(CH_2) - S\}_n$ does not.

DISCUSSION

Although these observations may be of interest to the spectroscopist or statistical thermodynamist, their interest to the polymer scientist centres on the connection between the *LA* mode frequency and the X-ray-determined long spacing. This is understood in principle since it is known that

$$v_{LA} = \frac{m}{2l}\sqrt{\frac{E}{\rho}} \qquad (1)$$

where v = *LA* mode frequency, m = order of the vibration (and is an odd integer to satisfy Raman selection rules), l = the length of the acoustic vibrator, E = Young's modulus of the crystal along the 'c' axis and ρ = the density of the polymer chain. Hence one can determine from v the approximate 'stem length' of the chains in the lamellae. The value of E for polyethylene is known; hence the Raman technique is of value for this polymer in morphological studies[4]. In other cases, the value of E is unknown. Intuition suggests that it will be moderately large in planar molecules but that in all except polyethylene the density term will force v_{LA} to values so small as to be experimentally inaccessible. In helical polymers, the value of ρ would be moderately high and E will probably be unfortunately small. The recent observation of *LA* modes in poly(ethylene sulphide)[5] and isotactic polypropylene[6], however, suggests that this somewhat pessimistic forcast is exaggerated. Of the systems described in this paper, one is helical $\{(CH_2)_3 - S\}_n$ confirming the proposal that the value of E effective in helical systems is of the same order as that in planar ones.

LAXD data is available on poly(decamethylene oxide)[7] and poly(hexamethylene oxide)[8]. The authors described the thermal history of their specimens and we have duplicated these as far as possible before recording Raman spectra. If we *assume* identicality of our specimens and theirs, the value of E is fairly close that that in linear polyethylene (see *Table 2*). To confirm the proposition that a long run of methylene groups between backbone hetero atoms acoustically vibrates as if the hetero atoms were not present, we then studied poly(decamethylene sulphide). LAXD data were obtained on this specimen[10], confirming that the value of E in this case is again moderately close to that in linear polyethylene. A recent study of a low melting solid, poly (decamethylene sebacate), has also yielded similar results[9]. LAXD data have also been obtained on polytetrahydrofuran[10]. In this case, the value of E deduced from Raman data is in very poor agreement with that from linear polyethylene.

Thus to conclude it would appear that in *linear* polymers containing long runs of methylenic backbone species, their

Table 1 Low frequency Raman spectra ($\Delta\upsilon$ 150 cm^{-1}) of some polyethers and polythioethers

Sample	Treatment	Raman band frequencies, $\Delta\upsilon$ (cm^{-1})
Ethers		
$\{(CH_2)_4{-}O\}_n$	SC	~96, w,b ~59 w,b, †29 ms
	MQ	– – †30 ms
	MQ or SC/A 38°C	~96, w,b ~58 w,b, †20 s
$\{(CH_2)_6{-}O\}_n$	SC	~84 vw, ~64 vw, †31 s
	SC/A 48°C	~82 vw, ~63 vw, †19 ms
	MQ	~82 vw, ~63 vw, †25 ms
	MQ/A 52°C	– – †18 ms
$\{(CH_2)_{10}{-}O\}_n$	SC	78 w, †59 w, †32 s, †21 w,sh
	SC or MQ/A 75°C	†52 vw, †23 w, †12.5 s
	MQ	75 vw, †62 w, †29 s, †17 w,sh
	MQ/A 64°C	64 w, †48 vw, †25 m, †15.5 s
Thioethers		
$\{(CH_2)_3{-}S\}_n$	SC	46 w, †16 s
	MQ	46 w, †13 s
	SC or MQ/A 62°C	46 w, †10 s
$\{(CH_2)_4{-}S\}_n$	SC	159 w, 69 w, †35 s
	SC/A 57°C	158 w, 71 w, †29 s
	MQ	159 w, 71 w, †32 s
	MQ/A 64°C	– ~74 w, †25 s
$\{(CH_2)_5{-}S\}_n$	SC	138 w, 59 w, †32 s
	SC/A 63°C	138 w, 59 w, †28 s
	MQ	138 w, 59 w, †28 s
	MQ/A 71°C	– – †23 s
$\{(CH_2)_6{-}S\}_n$	SC	120 m,b, 44 m, †28 s
	SC/A 68°C	120 m,b, 44 m, †24 s
	MQ	118–114 m, 44 m, 26 s
	MQ/A 76°C	120 m,b, 44 m, †21 s
$\{(CH_2)_{10}{-}S\}_n$	SC	154–148 w, 85–80 w,b, †29 s
	SC/A 72°C	– 89 w, 80 w, 76 w, †69 w, †21 s
	MQ	– ~116 w, ~80 w, ~76 w, ~69 w, †20 s
	SC or MQ/A 85°C	~150 w,b, 110 w, 90 w, 71 w, 59 vw, †16 s

SC, Solution crystallized from benzene or chloroform at room temperature; MQ, melted and quenched into cold water; /A x°C annealed for 3 h at x°C; † bands which satisfy the 'rules' for *LA* mode behaviour. In some cases, a number of bands appear to satisfy the criteria for an origin in acoustic vibrations. This may be due to the appearance of higher order vibrations. The lowest observed band is taken as the fundamental (i.e. $m = 1$ in equation 1). In solution–crystallized $[(CH_2)_{10}O]_n$ we relate the bands at 32(SC) and 12.5 (75°C) on the evidence of their intensity.

Table 2 Young's Moduli of PDMO, PHMO and PMDS as deduced from Raman spectra and LAXD data

Sample	Primary *LA* mode frequency $\Delta\upsilon$(cm^{-1})	LAXD long spacing (Å)	*E* (dyne/cm^2) X 10^{12}
$\{(CH_2)_{10}-0\}_n$	32	102 (7)	4.5*
$\{(CH_2)_6-0\}_n$	31	100 (8)	4*
$\{(CH_2)_{10}S-\}_n$	29	110 (10)	4.27

E calculated using simple equation given in text. *E* for polyethylene $3.58 \pm 0.25 \times 10^{12}$ dyne/cm^2 [11].

* Since the identicality of samples used in the Raman and X-ray studies is not definite we claim low precision in these cases.

acoustic vibrational behaviour is close to that of polyethylene. This then enables us to use the crystalline Young's modulus for polyethylene and hence to calculate very approximate thicknesses of crystalline lamellae by a new and independent route. In one case, $|(CH_2)_{10}|_n$, more precise estimations may be made as an accurate value of *E* is known. As pointed out before[5], however, in any polymer, *changes* of thickness can be monitored precisely even though *E* is known only approximately.

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