Letters

A Report on the longitudinal accordian mode in polyalkenamers using low frequency Raman spectroscopy

Polyalkenamers have the repeat unit $+CH{=}CH{-}(CH_2)_m+$ and hence may be regarded as higher homologues of *trans* 1,4 polybutadiene $+CH{=}CH{-}(CH_2)_2+$. Because polyalkenamers contain methylene sequences, they also have a structural similarity to polyethylene $+CH_2+_m$ and to the normal paraffins $CH_3{-}(CH_2)_m{-}CH_3$.

Wide-angle X-ray diffraction has shown that the methylene sequences in polyalkenamers[1] have a *trans* conformation as in crystalline polyethylene and normal paraffins, while the conformation about the double bond is skew (+120°), *trans*, skew (−120°) as in *trans*-1,4-polybutadiene[2].

Examination of polyalkenamers using the electron microscope has revealed that chain-folded lamellar crystals can be grown from solution[3]. It was established that for a given member of the series it is possible to make samples with different crystal thicknesses by varying the crystallization temperature[3]. The work being reported in this paper was carried out on samples of polyoctenamer (m = 6), polydecenamer (m = 8) and polydodecenamer (m = 10) which were prepared using this method.

As part of a wider programme of research into polymer crystallization we have been examining the scope and limitations of the use of Raman spectroscopy to measure lamellar thickness. This is made possible by the observation of the longitudinal accordion mode, or *LAM*, whose frequency in the case of the normal paraffins[4] C_nH_{2n+2} varies as the reciprocal of n. As documented elsewhere[5,6,7] the frequency of the *LAM* in the case of polyethylene gives a measure of the lamellar thickness.

Currently there is a debate on how chain-defects perturb the *LAM* and how these perturbations influence the Raman value of lamellar thickness. Interest in the Raman spectra of polyalkenamers arises, therefore, because they afford an opportunity to examine the effect on the *LAM* frequency of introducing double bonds into a *trans* methylene chain. The preparation procedures used in this work and the method of obtaining the Raman spectra were the same as used in earlier works[3,7].

A criterion for establishing that a band is a *LAM* of chains which traverse the lamellae is that its frequency should vary with lamellar thickness. Lamellar thicknesses were determined by small-angle X-ray diffraction. The lamellar thicknesses of the samples varied from 100 to 175 Å. One would expect the corresponding *LAMs* to be in the region of wavenumber shifts $\Delta\tilde{\nu}$ = 31–18 cm^{-1}, using normal paraffins as a rough guide[4,5,6]. We scanned from as close to the laser line as possible (usually $\Delta\tilde{\nu}$ = 8 cm^{-1}) up to wavenumber shifts of 500 cm^{-1}. A band was found at $\Delta\tilde{\nu}$ = 22 cm^{-1} in samples of both polydodecenamer and polydecenamer. It was of similar intensity to the *trans* carbon–carbon double bond stretching frequency at $\Delta\tilde{\nu}$ = 1670 cm^{-1}. The band at $\Delta\tilde{\nu}$ = 22 cm^{-1} showed no variation in wavenumber shift with lamellar thickness. A weaker band at $\Delta\tilde{\nu}$ = 50 cm^{-1} was also found in all samples of polydodecenamer and polydecenamer. By the criterion just described neither of these bands can be assigned to a *LAM* of the chains which traverse the lamellae. By comparison with the low-frequency spectrum of *trans*-1,4-polybutadiene[2] it seems more likely that the bands at $\Delta\tilde{\nu}$ = 22 and 50 cm^{-1} are lattice modes. The assignment of these bands and others in the region $\Delta\tilde{\nu}$ = 500–2000 cm^{-1} will be discussed further in a separate publication.

When the region near $\Delta\tilde{\nu}$ = 200 cm^{-1} was scanned, each polyalkenamer was found to have a band, whose frequency depended upon the number of carbon atoms in the repeat unit $+C_nH_{2n-2}+$ of the polyalkenamer. As shown in the table the wavenumber shift decreases with increasing n and hence fulfills the criterion for a *LAM*, not of the whole chain traverse, but of the repeat unit. In support of this suggestion it will be seen that the wavenumber of this band is quite close to the *LAM* wavenumber shift of the crystalline paraffin (C_nH_{2n+2}) which has the same number of carbon atoms, n.

It must be noted that octane (n = 8), decane (n = 10) and dodecane (n = 12) are liquids whilst the polyalkenamers are solids at room temperature. It has been reported[8] that paraffins with $n < 9$ such as octane have a *LAM* at similar frequencies in both the solid and liquid states. Whereas when $n \geqslant 9$ as in decane and dodecane the *LAM* corresponding to the all-*trans* conformation is observed only for the solid state. It has been concluded[8], therefore, that the all-*trans* conformation is energetically favourable for solid and liquid paraffins when $n < 9$ but for solid paraffins only when $n \geqslant 9$, This has the consequence that the comparison of the spectra of polydecenamer and polydodecenamer taken at room temperature with those of decane and dodecane respectively taken at lower temperatures is not unreasonable, because one may infer that the methylene sequences are all-*trans* throughout.

One may think of the polyalkenamers in terms of the interruption that a double bond presents to the propagation of the *LAM* vibration along the chain. Firstly, if one assumes

Table 1 Comparison of the low frequency Raman spectra of polyalkenamers and normal paraffins

	Polyalkenamers	Normal paraffins*	
		$CH_3{-}(CH_2)_m{-}CH_3$ C_nH_{2n+2}	
n	$+CH{=}CH{-}(CH_2)_n+$ $+C_nH_{2n-2}+$	Solid	Liquid
8	284 cm^{-1}	282 cm^{-1}	283 cm^{-1}
10	230 cm^{-1}	230 cm^{-1}	–
12	188 cm^{-1}	195 cm^{-1}	–

* Data taken from references 8 and 9 for solids at 168K and liquids at 297K. Data for the polyalkenamers taken from spectra recorded at room temperature

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that values of force constants for smaller molecules[10] can be transferred to polyalkenamers then there would be an approximately two-fold increase in force constant at the double bond. Secondly, the introduction of a double bond brings about at conformational change to skew (+120°), *trans*, skew (−120°). This lateral displacement of the chain at the double bond[1] may be regarded as a type of defect. It is to be noted that calculations[11] have indicated that the *LAM* corresponding to the whole chain traverse is greatly reduced in intensity when conformational defects are introduced into an all-*trans* chain. We would suggest that these two effects in conjunction could be responsible for decoupling the *LAM* at the double bond in polyalkenamers.

In summary, therefore, we looked for, but did not find, a *LAM* corresponding to the thickness of polyalkenamer lamellae. However, a band has been found which displays the characteristics of a *LAM* of the repeat unit of a polyalkenamer. From this we conclude that the *LAM* may be decoupled by double bonds. This conclusion is in line with an observation made elsewhere[12] that in salts of an unsaturated dicarboxylic acid two *LAM*s are seen which are characteristic of the lengths of chain on either side of the double bond. Similarly, by comparison with normal paraffins, it appears that in polyalkenamers the *LAM* gives a measure of the number of carbon atoms in the repeat unit of the polymer.

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Evidence for crystallinity in poly(ether sulphone)

Certain polymers appear to be incorrigibly non-crystalline and are customarily described as amorphous. The stiff, bulky chains of poly(ether sulphone), (PES), constitute a severe challenge to any attempt to produce an ordered structure. Direct crystallization has so far failed but other approaches are possible. Some polymers, including poly(ethylene terephthalate), are prone to solvent-induced crystallization and this has been well documented in recent years[1]. PES must now be added to the list of polymers which can develop crystallinity with the assistance of a solvent.

Recent work[2,3] has shown that the systems formed by PES and organic solvents are exceedingly complicated with features including lower critical solution temperatures, gelation and solvent-induced resistance. The last mentioned feature led directly to the discovery of crystallinity in a sample. In the course of experiments on the kinetics of dissolution of PES in organic solvents[2,3] it was noted that the polymer could be made virtually insoluble in dichloromethane by a previous controlled encounter with the same solvent. This strongly suggested that a crystalline structure was being produced and the conclusion was confirmed directly by X-ray diffraction as shown in *Figure 1* and *Table 1*. Solvent-resistant samples of the polymer could be obtained in a number of ways of which the following is typical.

A clear solution of the polymer was prepared at 40°C by dissolving some PES in four times its own weight of dichloro-

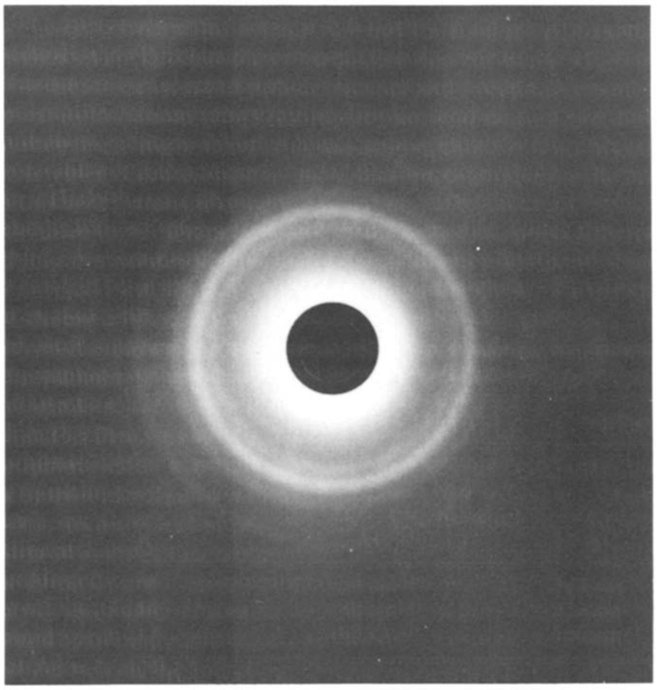

Figure 1 Typical X-ray diffraction pattern produced by polyethersulphone containing dichloromethane

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