Raman, infra-red and neutron studies of low frequency vibrations in some substituted polystyrenes

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The Raman, i.r. and neutron spectra of polystyrene in amorphous and partly crystalline isotactic forms are reported, together with similar data for polystyrene derivatives, in the frequency region below 560 cm^{-1}. The band at about 60 cm^{-1} in polystyrene is assigned to a phenyl group libration, and there is evidence of increased steric hindrance in the case of *ortho* substitutions to the phenyl group. The band at 20 cm^{-1} is unaffected by substitutions and may arise from acoustic vibrations. Earlier assignments of certain i.r. and Raman bands in the range 140–560 cm^{-1} are generally supported by the present measurements on polystyrene derivatives, but there is no indication of the C–X out of plane bending vibration, 10b, coupling with deformations of different backbone conformations. The absence of a band corresponding to backbone motion near 200 cm^{-1} implies that wavevector selection rules are not relaxed in this region.

INTRODUCTION

Much interest has recently been generated in the low frequency spectra (<100 cm^{-1}) of solid amorphous systems. Inorganic glasses have been extensively studied and relationships established between Raman data and density of states functions for both amorphous[1–6] and crystalline systems[7]. The importance of the low frequency data in relation to fundamental thermodynamic properties has also been shown[7–10]. Progress with synthetic organic polymers has generally been limited to specific problems including the study of longitudinal acoustic excitations in lamellar crystals[11–13]. Assignments of low frequency modes in amorphous polymers are few in number[14,15] though such work is clearly relevant to the relaxational properties of the polymers. There also remains considerable scope for developing relationships with thermodynamic parameters[16,17]. In the present paper we examine in detail the low frequency motions of polystyrene (PS) using Raman, i.r. and neutron techniques.

Low frequency Raman data for solid atactic polystyrene and poly(methyl methacrylate) have previously been reported[18], showing in each case broad bands at about 20 and 60 cm^{-1}. The molecular weight dependence of these bands was investigated for polystyrene, but an attempt to explain these results on the basis of skeletal normal mode calculations, using a simplified chain model, proved to be unsuccessful[18].

In order to obtain more information about these low frequency vibrations, Raman, i.r. and neutron measurements were made on polystyrene derivatives with chemical substitutions in the phenyl group. These results are reported here, and the frequency range of the Raman experiments has been extended to 560 cm^{-1} to include bands which have been assigned by Jasse and Monnerie on the basis of i.r. and Raman studies of the polystyrene model compounds, 2,4-diphenylpentane and 2,4,6-triphenylheptane[19]. These authors assigned bands at 216 and 410 cm^{-1} in the Raman spectrum of polystyrene respectively to a C–X in-plane bending vibration and an out-of-plane mode of the phenyl group 'skeleton'. Similarly, bands at 152 and 196 cm^{-1} were assigned to a C–X out-of-plane vibration coupled to a chain deformation involving some *gauche* conformations and totally *trans* conformations respectively. In all cases the interpretations were in terms of the approximate forms of vibrational modes for monosubstituted benzene, although the vibrational forms illustrated (Table 2 of ref 19) apply only to benzene itself. It is therefore of interest to discover whether changes in the Raman spectra caused by chemical substitutions within the phenyl group are consistent with this interpretation. In addition, the normal mode calculations mentioned earlier showed peaks in the density of states functions for two acoustic branches in the region of 200 cm^{-1}. Mode assignments in this region also require inspection; if the bands can all be attributed to side group vibrations it would suggest that, subject to the accuracy of the normal mode calculations, the wavevector selection rules are not relaxed. The low frequency Raman spectrum of partially crystalline, isotactic polystyrene was also reported earlier[18], and further data obtained at 295 and 100 K are presented here.

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Neutron scattering measurements were also made of the vibrational density of states of isotactic poly(styrene-H_8) and poly[CD_2–$CD_2(C_6H_5)$]. These gave additional support to the assignment of vibrations to phenyl group and backbone vibrations. In addition the i.r. absorption was measured for some of the substituted samples‡.

EXPERIMENTAL

A series of substituted atactic polystyrene samples were provided by Professor L. Monnerie of the Laboratoire P.C.S.M., Paris. The samples used for Raman measurements were polyfluorostyrenes with substituents in the *meta* and *para* positions, poly(*p*–bromostyrene), poly(*p*–chlorostyrene) and polymethylstyrene with alpha- and *meta*-substitutions. These samples were all prepared by free-radical polymerization at 60°C using azobisisobutyronitrile as initiator, and the number-averaged molecular weights, $\bar{M}_n$, were reported to be within the range 10^5–10^6.

Dr R. H. Mobbs of the Chemistry Department, Manchester University, prepared *ortho*-substituted samples of polybromostyrene, polychlorostyrene and polyfluorostyrene by thermal polymerization. After reprecipitation, molecular weight determinations were made, using g.p.c. measurements, and in each case $\bar{M}_n$ was found to be about 3×10^4.

A sample of poly(vinyl toluene) in the form of a solid block, was thermally polymerized from a mixture of the *meta*- and *para*-substituted monomers in the proportions 60:40 by wt by Dr A. Hallam of the Physics Department, Manchester University. The material was polymerized for two weeks, to obtain a molecular weight within the range 10^5–10^6. A block of the polymer, with dimensions about 1 x 1 x 1 cm was cut out and polished with ICI 'Perspex' polish for use in Raman scattering experiments.

Dr H. N. Beck of the Dow Chemical Co. supplied a partly crystalline sample of isotactic polystyrene, with a molecular weight reported to be 3.8–3.9×10^6. A Soxhlet extraction was performed on this polymer, for 50 h, using butanone. This was found to decrease the proportion of atactic material, as indicated by ^{13}C n.m.r. measurements. To improve the optical quality of the sample, dissolution of the polymer in boiling *o*-dichlorobenzene was followed by reprecipitation from excess methanol. A thin film was prepared by pressing the washed and dried sample at 150°C and 7 tons/in^2 for 30 min between PTFE sheets. The crystallinity of this sample, determined by powder X-ray diffraction measurements (for details of the method, see ref 20) was found to be 37 ± 2%. The isotactic polystyrenes used for the neutron experiments were prepared by Dr P. J. Tait of University of Manchester Institute of Science and Technology using a $TiCl_3/Al(i\text{-}Bu)_3$ catalyst in benzene. Fractions soluble in toluene but insoluble in methyl ethyl ketone were used as samples. Nuclear magnetic resonance spectra were taken to confirm the tacticity[21]. For i.r. work, samples of poly(*ortho*-fluoro-chloro- and bromo-) styrene of thickness ~0.1 mm and area ~5 cm^2 were prepared by evaporation from chloroform solution.

Raman measurements at room temperature on all the halogen and methyl substituted polystyrene samples were made with the powders pressed into a tapered hole drilled in a steel cylinder. Low temperature measurements were made on films of thickness about 1 mm obtained by pressing the powdered samples at just sufficiently high temperatures to produce adequate optical quality. However, the quality was still not good enough to allow the use of polarized Raman scattering experiments as an aid to band assignment. A Cary 82 triple grating Raman spectrometer was used for all these measurements, and the exciting line was the 5145 Å line of a Spectra Physics 164 Argon ion laser. In all cases, the conventional 90° scattering arrangement was adopted. Details of measurements at liquid nitrogen temperatures have previously been given[18].

The neutron spectra were recorded using the 6H and 4H5 cold neutron time of flight spectrometers at AERE Harwell[22]. The sample, an identical sample container and a standard vanadium plate were enclosed in an evacuated chamber and cycled periodically through the neutron beam during the experiments. Spectra at a range of angles $< 90°$ were collected simultaneously. All results were taken at ambient temperature. After the scattering from the sample container had been subtracted from the raw data, the vanadium scattering data were used to normalize the results from the different detectors and to calculate the double differential cross-section $d^2\sigma/d\Omega dE$, for each scattering angle. Through standard manipulations an amplitude weighted density of states $\rho(\omega)$, and a closely related approximation to this, $\Sigma[S(Q,\omega)/Q^2]$, can be obtained[23].

RESULTS

Raman and infra-red

Fluorescence problems with certain samples prevented the collection of data at 100K. For this reason the spectra of fluorine derivatives shown in *Figure 1*, were taken at a

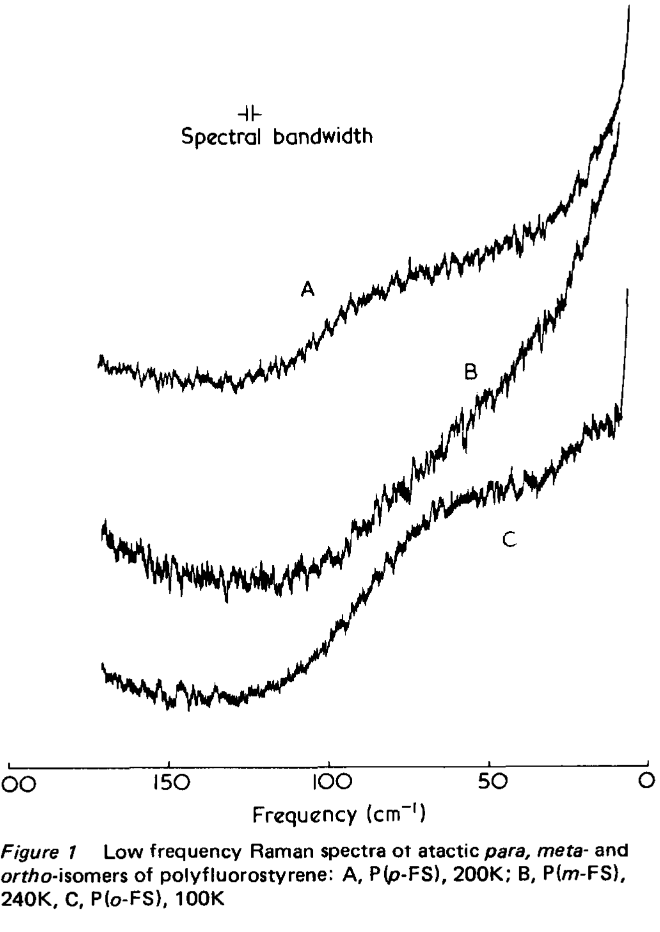

Figure 1 Low frequency Raman spectra of atactic *para*, *meta*- and *ortho*-isomers of polyfluorostyrene: A, P(*p*-FS), 200K; B, P(*m*-FS), 240K, C, P(*o*-FS), 100K

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‡ The i.r. measurements were made by Dr P. Brier and Mr. D. Farnsworth of the Chemistry Department, Manchester University

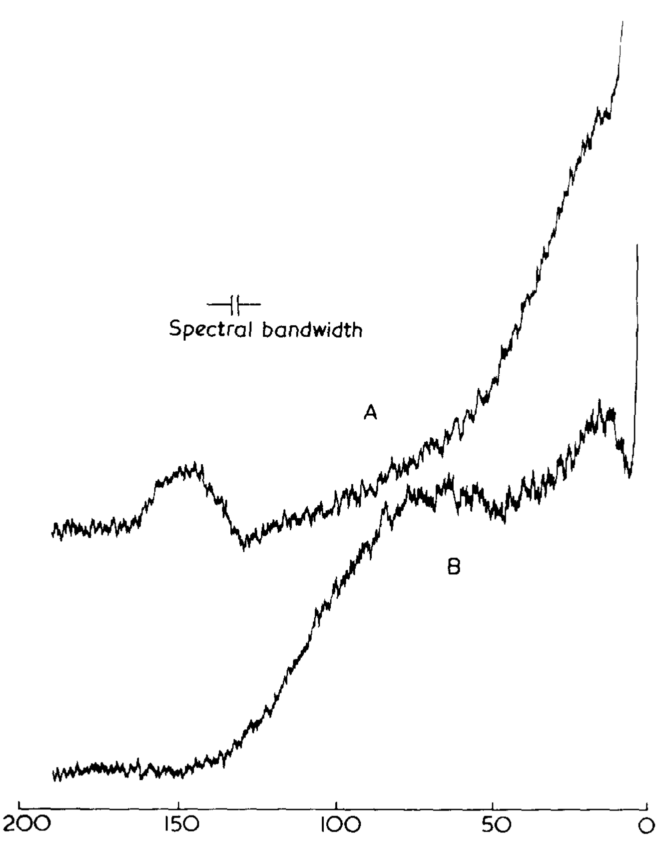

Figure 2 Low frequency Raman spectra of atactic polystyrene and poly(*o*–bromostyrene) at 100K: A, P(*o*-Brs), 100K; B, PS, 100K

variety of temperatures. In spite of this difficulty these spectra show a clear variation of the band near 60 cm^{-1} in polystyrene with substitution site.

Figure 2 compares the Raman spectra of polystyrene itself and poly(*o*-bromostyrene). The broad band at 144 cm^{-1} for poly(*o*-bromostyrene) will be considered later, as will be the 226 cm^{-1} band in the spectrum of poly(α-methylstyrene) (*Figure 3*).

It is evident from *Figures 1* to *3* that the determination of peak frequencies in this region is made difficult by the overlapping of Raman bands. Nevertheless, the Raman spectra of all the samples considered here clearly showed that there was no variation, within experimental errors, in the 20 cm^{-1} Raman band. As a first approximation in obtaining the 60 cm^{-1} band shape it was assumed, then, that the 20 cm^{-1} band shape was independent of substitution. The temperature dependence of the intensity of both 20 and 60 cm^{-1} bands has been shown to be first order in the range 125–250K[18]; i.e. no deviations are observed from Bose population predictions. Thus it was possible to calculate the shape of the 20 cm^{-1} polystyrene peak appropriate to the temperature at which the various substituted spectra had been taken, using data obtained at 100K. These band shapes were then subtracted from the full spectra to give the 60 cm^{-1} band shape. The Raman spectrum of each substituted polymer at very low frequencies (below about 10 cm^{-1}) was assumed to include no contribution from the 60 cm^{-1} band. The subtraction process implicitly assumes that the quasi-elastically scattered intensity is identical for each polymer, but this assumption has comparatively little effect on the peak position of a band around 60 cm^{-1}. Each spectrum was then corrected to a reference temperature of 300K, again assuming a first order temperature dependence.

Clearly, this treatment of the experimental data does not provide a precise determination of peak frequencies. However a comparison of the 20 cm^{-1} band shape obtained for polystyrene itself (see Figure 2 of ref 17) with the Raman spectrum of poly(*o*-bromostyrene), shown here in *Figure 2*, provides some justification for the procedure used: the poly(*o*-bromostyrene) sample has a very weak Raman band around 50 cm^{-1}, and the much more intense peak at 20 cm^{-1} shows great similarity in band shape with the corresponding feature in the polystyrene Raman spectrum. The i.r. measurements did not help to improve the accuracy of determinations of the peak positions. The data confirm the presence of a broad feature ~60 cm^{-1}, but could not be extended to low enough frequencies to observe the region around 20 cm^{-1}.

The Raman peak frequencies obtained in this way are plotted in *Figure 4* against side-group mass. The error bar provides an indication of the uncertainty involved in determining peak frequencies from the Raman data. The frequency dependence expected from two simple modes of side-group vibration is also shown in *Figure 4*. A simple model of a mass, m, vibrating on a mass-less spring, leads to the relationship between frequency, ω, and mass, m, of $\omega \propto m^{-1/2}$, and the application of this model requires that the side-group should be rigid, and that the carbon–carbon bond stretching force constant involved, should be insensitive to substitution. For a phenyl group torsional vibration, about the bond connecting the side-group with the backbone, the torsional frequency is proportional to $I^{-1/2}$, where I is the moment of inertia of the rotating group about the axis of rotation. For each polymer, the axis of rotation was assumed to pass through the centre of mass of the phenyl group. Provided that the potential for phenyl group rotation is independent of substituent character, then any frequency shift should be attributable to changes in I alone. Calculations of the potential barrier to phenyl group rotation in syndiotactic polystyrene indicate that, for the most probable backbone conformations, the amplitude of phenyl group rotation is restricted to ±20–30° about the equilibrium position[24].

Figure 5 shows the low frequency Raman spectrum of the partially crystalline isotactic polystyrene sample. The background fluorescence is noticeable at 100K.

Examples of Raman data obtained within the frequency range 100–600 cm^{-1} are given in *Figure 6* and results for all the substituted samples are presented in *Table 1*. Infra-red

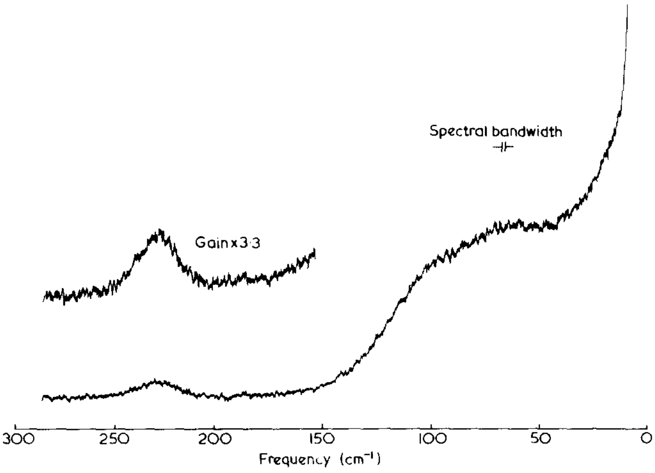

Figure 3 Room temperature Raman spectrum of poly(α-methylstyrene)

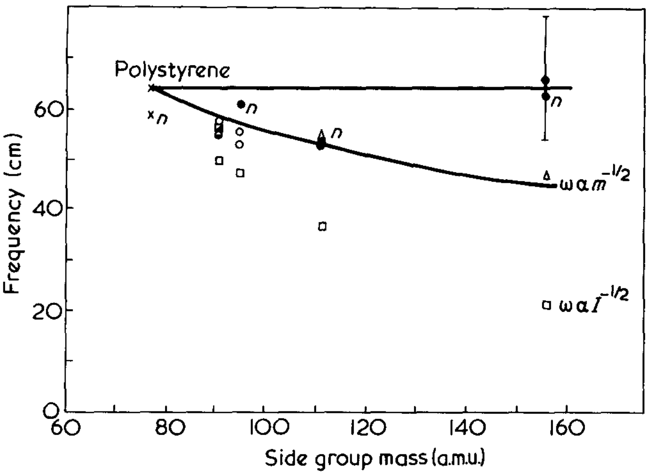

Figure 4 Frequency shifts in the 60 cm^{-1} band in polystyrene with variation in side-group mass. Neutron data are denoted *n*; the other data are from Raman spectra. Experimental results are shown for X-polystyrene: △, *ortho*-; ○, *meta*-; ●, *para*-derivatives; ◒, poly(vinyl toluene). Theoretical values are plotted for a phenyl group torsional vibration: □, corresponding to *ortho*- and *meta*-derivatives; ◪, poly(vinyl toluene); horizontal line, *para*-derivatives. The curve labelled $\omega \propto m^{-1/2}$ represents the expected frequency dependence for a simple 'mass on a spring' model

data are also included in this Table. The strongest of these are bands in the region 440–500 cm^{-1}.

Inelastic neutron scattering

Neutron spectra have been recorded of the isotactic polymers of styrene (CD–CD_2) styrene and *para*-fluorostyrene and of the atactic polymers of styrene, *para*-fluoro-, *para*-chloro- and *para*-bromo-styrene. When the data had been converted to the form of an amplitude weighted frequency distribution it was found that all the spectra exhibited a principal feature at approximately 60 cm^{-1} (see *Table 2*). There were other features at 250 and 30 cm^{-1}. The spectra of the partly and the non-deuterated isotactic polystyrenes showed that in the former the 250 cm^{-1} band had disappeared and that the intensity at 30 cm^{-1} band was smaller relative to the principal band (*Figure 7*). It is reasonable to suppose that the bands of reduced intensity in the partially deuterated compound could be ascribed to vibrations that do not involve the phenyl group.

DISCUSSION

0–150 cm^{-1}

The lack of any significant variation in the 20 cm^{-1} Raman band on making substitutions in the phenyl group was noted earlier. However, the 60 cm^{-1} band is generally found to decrease in intensity with increasing side-group mass. This effect is particularly marked in the case of poly(*o*-bromostyrene) (*Figure 2*) and provides a strong indication that the vibration primarily involves side-group motion. Generally, the band intensity is significantly reduced by *ortho*-substitution, as compared with the effect of *meta*- or *para*-substitution, although this result is not observed for relatively light substituents; for polyfluorostyrene, the band intensity is smallest for substitution in the *meta*-position (*Figure 1*). The general result probably reflects the more restricted vibrational amplitude in *ortho*-substituted polystyrenes, due to steric hindrance. Calculations have shown that, for example, the barrier to phenyl group rotation is indeed expected to increase considerably on substitution in the *ortho* position[24]. The anomalous results for polyfluorostyrene may be due to the relatively short C–F bond length (~1.35 Å); in this case a different steric interaction may be responsible for restricting the phenyl group motion.

The frequency values are plotted in *Figure 4* together with their predicted dependence for the model of a mass vibrating on a spring. It can be seen that most of the Raman data points fall on the predicted line except that for poly(*p*-bromostyrene). However, it is important to note that the neutron results confirm the vibrational frequency found for this molecule (see *Table 2*). Agreement with the frequency dependence expected for a torsional vibration about the bond linking the side group with the backbone is

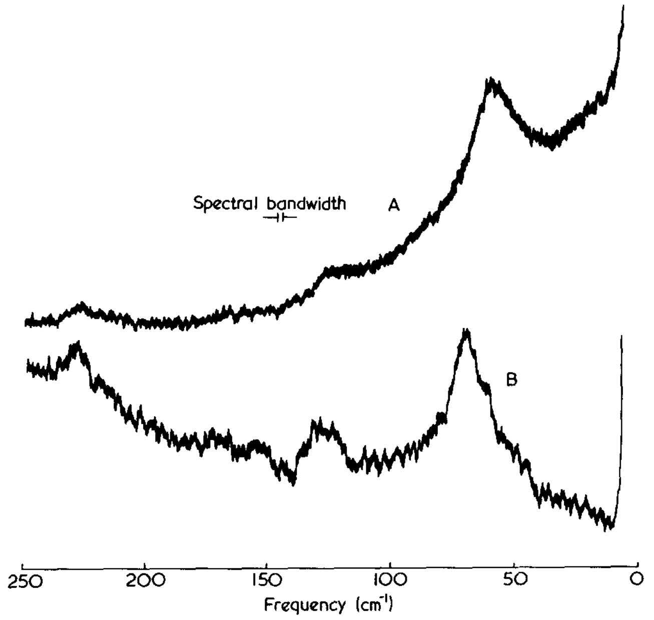

Figure 5 Low frequency Raman spectra of isotactic partly crystalline polystyrene at 295 (A) and 100K (B)

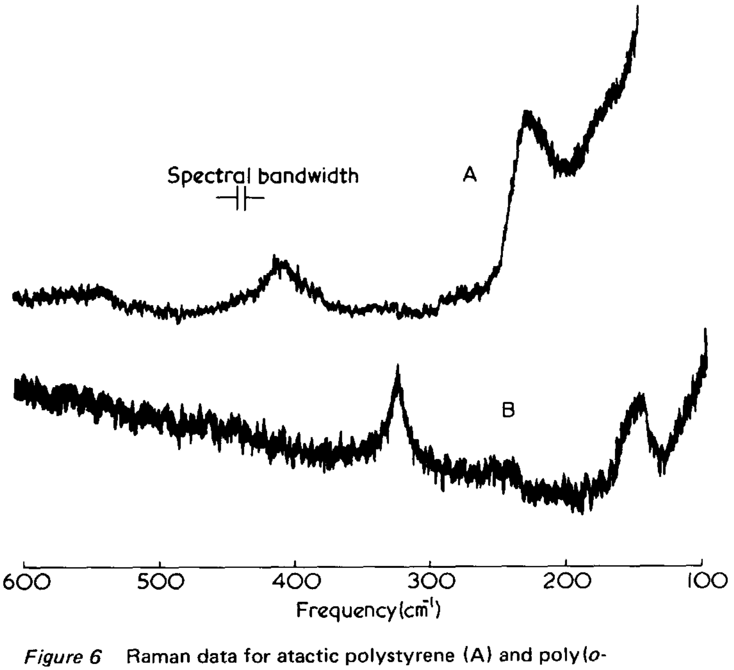

Figure 6 Raman data for atactic polystyrene (A) and poly(*o*-bromostyrene) (B) at room temperature

Table 1 Raman modes of polystyrene and its derivates within the range 150–560 cm^{-1} (Infra-red peaks shown in parentheses)

Sample	Infra-red and Raman frequencies (cm^{-1})						
PS	168(vw)(10b)	222(m) (9b)				407(w) (16a)	553(w)
P(*p*FS)	252(vw)(10b)	350(w) (9b)				426(vw)(16a)	
P(*m*FS)	212(vw)(10b)	247(m) (9a)				523(w) (16a)	
P(*o*FS)		177(m) (9a)	295(w)(10a?)	(348)335(vvw)	(495)	507(vw)(16a)	(552)555(vw)
P(*o*ClS)		155(m) (9a)	266(w)(10a?)	(414)413(m)	(457)	470(vw)(16a)	(552)
P(*o*BrS)		144(m) (9a)	253(w)(10a?)	321(m)	(447)		(552)
P(*p*BrS)	242(w)(10b?)	307(m) (9b)		335(m)			
P(*p*ClS)		323(vw) (9b)		361(vw)			
P(*m*MeS)		223(w) (9a)				525(w) (16a)	
PVT	201(m)(?) (*para*)	223(ms)(9a) (*meta*) 320(w)(9b) (*para*)		365(vw)		412(vw)(16a) (*para*) 525(m)(16a) (*meta*)	
P(αMeS)		226(m) (9b)		310(w)			
	I	II				III	

Nomenclature: w = weak, m = medium, s = strong, v = very, ? = tentative assignment. Vibrational mode notation is that adopted by Varsanyi[25].

Table 2 Principal features in the inelastic neutron spectra of various polystyrenes

	Energies (cm^{-1})		
Isotactic polystyrene	34	58	250
Isotactic polystyrene-d_4	26	54	–
Atactic polystyrene	34	58	250
Atactic poly(*p*-fluorostyrene)	33	60	250
Atactic poly(*p*-chlorostyrene)	–	54	250
Atactic poly(*p*-bromostyrene)	30	64	250

poor, although the torsional potential may be strongly dependent on the nature of the substituent. The small difference between the vibration frequency of polystyrene and poly(*p*-bromostyrene), however, does support the idea that the vibration may be a torsion. Further evidence that the band is due to a large amplitude vibration such as a torsion comes from the intensity of this band in the neutron spectrum. There is no other scattering at low frequencies of comparable intensity. For the simple model of an oscillator vibrating or librating against an infinite mass one can predict that the ratio of the intensity of these librations to the intensity of motions involving translation of the side group in the neutron spectrum would be 3:1 for polystyrene and 8:1 for poly(*p*-bromostyrene). These values will obviously be modified by mode mixing and dispersion but they do suggest that the intense band in the poly(*p*-bromostyrene) sample at least is associated with a torsion of the phenyl group. Unfortunately the large errors involved in frequency measurements prevent a firm assignment.

The higher peak positions found from the neutron spectra compared with those found from the Raman spectra for the lowest frequency band in polystyrene and its derivatives may reflect the vibrational amplitude weighting of the density of states that is observed in the neutron experiment.

The similar shape of the 60 cm^{-1} Raman band in polystyrene (*Figure 2*) and poly(α-methylstyrene) (*Figure 3*) also support its assignment to a side group vibration, although the intensity of the latter spectrum does not fall off so fast above about 70 cm^{-1}. In a speculative vein, it is suggested that two Raman bands in this region may be caused by the influence of the backbone conformation on phenyl group motion. For example, Tonelli has shown that, for phenyl group rotation in polystyrene about the bond connecting the side-group with the backbone, the equilibrium position of the phenyl ring plane for the most likely skeletal configurations bisects the backbone valence angle[24]. However, for the most probable backbone conformations of poly(α-methylstyrene) (*tttt*, ttg^+g^+, tg^+tg^+ and tg^-tg^-), the equilibrium position of the phenyl group was shown to be determined by the skeletal conformations involved. In the configurations *tttt* and ttg^+g^+, the plane of the phenyl ring again bisects the valence angle, but in the other two conformations the phenyl ring lies in the plane of this angle. These two conditions may, therefore, be expected to give rise to two different distributions of phenyl group torsional frequencies. Further Raman measurements on different stereoregular forms of poly(α-methylstyrene) are necessary in order to clarify the situation.

The low frequency Raman spectrum of partly crystalline polystyrene (*Figure 5*) differs from that of the atactic polymer (*Figure 2*) in several respects. First, weak bands are observed at 124 and 160 cm^{-1}. The latter feature may have the same origin as the very weak shoulder observed at 168 cm^{-1} in 'atactic' polystyrene, whereas the 124 cm^{-1} band may either be obscured by the broad 60 cm^{-1} band in the atactic polymer or be associated with the crystalline regions only. The 60 cm^{-1} peak itself appears greatly narrowed in crystalline polystyrene, and superimposed on a broader feature. One possible interpretation of this observation also involves the effect of different backbone conformations in that the crystalline phase may give rise to a narrow Raman peak for this side-group mode, whereas a broader peak is expected from phenyl groups in the amorphous region. Similarly, it may be possible to account for differences in the bandshape for amorphous 'atactic' polystyrene and amorphous isotactic polystyrene[18] in terms of the backbone configura-

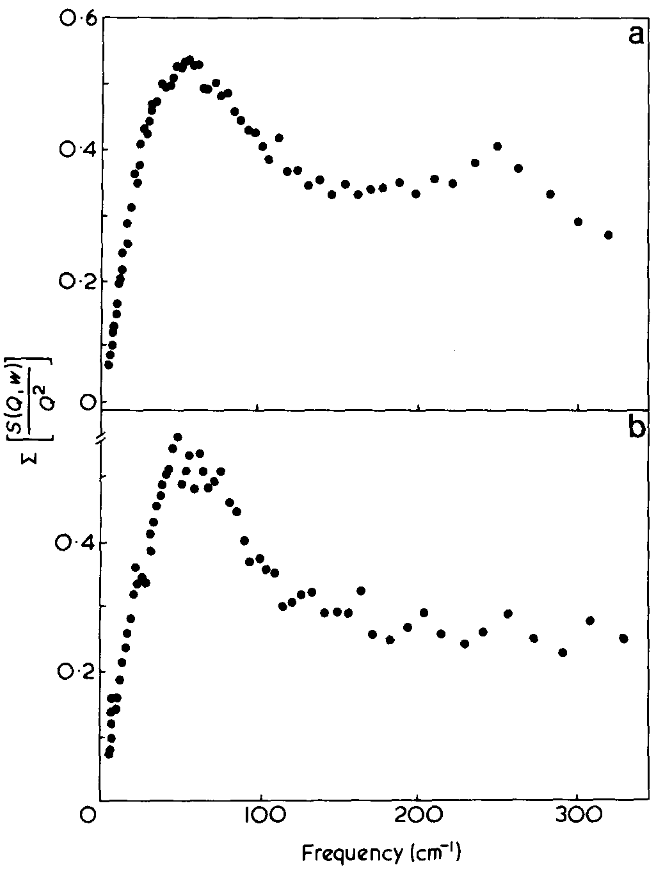

Figure 7 Inelastic neutron scattering data for (a) isotactic polystyrene and (b) isotactic polystyrene (CD—CD$_2$). The ordinate is $\Sigma[S(Q,\omega)/Q^2]$, an approximation to the amplitude weighted density of states

tions occurring in each polymer. Finally, the absence of any band in the region of 20 cm^{-1} is worthy of comment. It is not at present clear whether this is a result of more rigid wavevector selection rules operating in the case of the more highly ordered crystalline sample, or whether other vibrations are obscuring this feature. It is possible that atactic PS behaves in a similar manner to inorganic glasses in that disorder scattering gives rise to a broad Raman peak at low frequencies[6]. This requires further investigation.

The assignment of the 60 cm^{-1} Raman band in amorphous polystyrene to a phenyl group vibration has led to the application of Raman intensity measurements to the interpretation of low temperature specific heat data. One contribution to the non-Debye specific heat 'anomaly' was successfully isolated in this way[16] and a comparison with specific heat data for polystyrene derivatives lends qualitative support to this analysis[17].

140–560 cm^{-1}

Assignments by Jasse and Monnerie[19], summarized in the introduction, are taken as the starting point for a discussion of the results presented here in *Table 1*. These authors recorded Raman and i.r. spectra of 2,4-diphenyl-pentane and 2,4-triphenylheptane and found that the frequency of a band assigned to a C—X out-of-plane vibration was dependent on the configurational isomer. Earlier Raman data for polystyrene[26] were used to assign bands at 152 and 196 cm^{-1} to side-group vibrations coupled with motions characteristic of different backbone conformations. Krimm's work[26] contains a collation of previous Raman and i.r. measurements on polystyrene, and the 152 and 196 cm^{-1} bands listed referred to data obtained by Signer and Weiler[27] and Palm[28]. The former authors observed two bands below 500 cm^{-1}, these appearing at 196 and 211 cm^{-1}. Palm used a sample carefully polymerized to avoid impurities, and a feature at 152 cm^{-1} was the only Raman peak observed in this frequency region[28]. In view of the inconsistency of these results, the presence of Raman bands at 152 and 196 cm^{-1} must be in some doubt. The spectrum of polystyrene shown here (*Figure 2*) indicates only a Raman band at 222 cm^{-1} and a very weak shoulder at 168 cm^{-1}. Another study using laser excitation[29] showed similar results, but neither feature was assigned. It therefore seems highly improbable that the two bands at 152 and 196 cm^{-1} are genuine.

A comprehensive review of vibrational assignments for benzene derivatives has been made by Varsanyi[25], and this review has been used extensively in considering the validity of previous Raman band assignments for polystyrene. First, the out-of-plane phenyl group vibration of a mono-substituted benzene derivative, labelled 16a in Varsanyi's notation, generally appears as a very weak Raman band between 400 and 420 cm^{-1}, whereas the analogous 16b vibration occurs within the interval 430–570 cm^{-1} and also gives rise to a weak Raman band. The appearance of a strong i.r. band in this frequency range is consistent with this interpretation. Schematic representations of both vibrations have been produced by Whiffen[30]. In view of the frequency ranges quoted above, the assignment of the 407 cm^{-1} Raman band in polystyrene to be 16a vibration appears justified. The 553 cm^{-1} band falls within the range for 16b vibrations, but the frequency seems unusually high for such a massive substitutent.

For *para*-disubstitution, the 16a vibrational frequency is expected to be similar to that for mono-substituted derivatives, and the 426 cm^{-1} band in poly(*p*-fluorostyrene) is therefore assigned to this vibration although no bands in the corresponding chlorine and bromine substituted polymers are observed within the usual ranges for 16a and 16b vibrations. This may be a reflection of the poor optical quality and large fluorescence signals obtained with these latter samples. 16a vibrational frequencies for *meta*- and *ortho*-disubstitution are expected to be greater than the 16a frequency for a mono-substituted benzene. Bands at 523, 525 and 525 cm^{-1} in poly(*m*-fluorostyrene), poly(*m*-methylstyrene) and poly(vinyl toluene) are therefore assigned to the 16a vibration, the masses of the fluorine atom and methyl group being similar. 16a bands are at slightly lower frequencies for *o*-disubstitution, and bands at 507 and 470 cm^{-1} in the fluorine and chlorine derivatives are again assigned to 16a vibrations, although no corresponding band for poly(*o*-bromostyrene) was observed. A very weak band at 412 cm^{-1} in poly(vinyl toluene) was attributed to the 16a vibration of *para*-substituted phenyl groups, its intensity being less than the equivalent peak for *meta*-substitution, at 525 cm^{-1}. The absence of a peak around 400 cm^{-1} in polymethylstyrene is again probably due to the poor optical quality of the sample. It is to be regretted that this poor quality also precludes the use of depolarization ratio measurements as an aid to assignment.

The assignment of the 407 cm^{-1} Raman band in polystyrene to a 16a vibration is therefore supported by frequency shifts observed in these derivatives. The 16a vibrations are linked by the line labelled III in *Table 1*.

C—X in plane bending vibrations will now be considered. The frequency range for the 9b vibration in mono-substituted benzenes is from 200 to 410 cm^{-1} the mode frequency generally increasing with decreasing side-group mass. The corresponding vibrations for disubstituted derivatives may involve all the phenyl group carbon atoms moving in phase, or alternatively they may move in opposite phase (out-of-phase modes). For *para*-disubstitution, the 9b vibration (255–460 cm^{-1}) is in-phase and the 15 vibration (190–350 cm^{-1}) is the out-of-phase analogue, the 9b vibration giving the stronger Raman band. In *meta*-disubstitution, the 9a vibration is now the out-of-phase motion, occurring between 170 and 360 cm^{-1} as a strong Raman band. Mode 15 is the in-phase vibration (260–480 cm^{-1}). For *ortho*-disubstitution, the 18a vibration is the in-phase mode (250–450 cm^{-1}), appearing as a stronger Raman band than the 9a out-of-phase vibration (135–330 cm^{-1}).

The most intense Raman band in polystyrene, within this frequency range, is at 222 cm^{-1}, corresponding to the band at 216 cm^{-1} which has previously been assigned to the 9b vibration of a monosubstituted benzene derivative[19]. Noting that the out-of-phase vibration in disubstituted benzenes corresponding to this mode is generally a strong Raman band, the line II in *Table 1* links the most intense bands observed in the spectrum of each sample. These all have similar bandshapes. The band position in poly(α–methylstyrene), at 226 cm^{-1}, is almost identical to that for polystyrene indicating that the vibration is probably not of skeletal origin and supporting its assignment to 9b. Bands at 247 and 223 cm^{-1} in poly(*m*-fluorostyrene) and poly(*m*-methylstyrene) fall within the expected frequency range for 9a vibrations, and previous measurements on *meta*-disubstituted benzenes indicate that the frequency is expected to be higher for fluorine than for methyl substituents[25]. The majority of phenyl groups in poly(vinyl toluene) are *meta*-substituted, so the most intense 9a band is expected to occur around 223 cm^{-1}, which is indeed the case. Bands at 177, 155 and 144 cm^{-1} in the *ortho*-substituted samples of polyfluorostyrene, polychlorostyrene and polybromostyrene are assigned to the 9a vibration, the frequency for the bulky bromine substituent being particularly near to the lower limit of the range. In *para*-disubstituted benzene derivatives, the out-of-phase vibration 15 corresponds to a weaker Raman band than does the in-phase vibration 9b. Moreover, the 15 vibrational frequency is expected to be only slightly higher than that for the 9a vibration in the corresponding *m*-disubstituted compound. It is clear from *Table 1* that often no Raman band satisfies this condition and out-of-phase vibrations are therefore left unassigned. However, the 9b vibrational frequency is expected to be similar to that of the monosubstituted derivative with the lighter substituent[25]. 9b vibrations at about 410 cm^{-1} in fluorobenzene and 346 cm^{-1} in toluene[25] are therefore used to assign bands at 350 and 320 cm^{-1} in poly(*p*-fluorostyrene) and poly(vinyl toluene) to the 9b modes of the *para*-substituted forms. The 320 cm^{-1} band in the latter compound is weaker than the 223 cm^{-1} band, probably reflecting the smaller proportion of *meta*-disubstituted groups. Bands observed at 307 and 323 cm^{-1} in poly(*p*-bromostyrene) and poly(*p*-chlorostyrene) are similarly assigned to 9b vibrations.

The results discussed above support the assignment of the 222 cm^{-1} Raman band in polystyrene to the C–X in-plane bending vibration 9b.

Lastly C–X out-of-plane bending vibrations will be considered. For a monosubstituted benzene with a ‘heavy’ substituent, the schematic form of vibration 10b has been previously reported[31], and the frequency range is from 140 to 200 cm^{-1}, this range being extended to 250 cm^{-1} if the similar 17b vibration of monosubstituted benzenes with ‘light’ substituents is considered[25]. The vibration gives rise to a fairly strong Raman band. In *para*-disubstitution involving at least one ‘heavy’ substituent, the corresponding in-phase and out-of-phase vibrations are vibrations 11 and 10b, with respective frequency ranges of 80–220 cm^{-1} and 240–380 cm^{-1}. Few measurements have been made on vibration 11, because of instrumental difficulties previously experienced at low frequencies, but both bands are Raman active. For both *ortho*- and *meta*-disubstitution, where at least one ‘heavy’ substituent is involved, the in-phase mode approximates to vibration 10a and the out-of-phase vibration to 10b. The respective ranges for *ortho*-disubstitution are 171–298 cm^{-1} and 125–196 cm^{-1} and for *meta*-disubstitution 196–272 cm^{-1} and 126–235 cm^{-1}.

If the 168 cm^{-1} band in polystyrene is assigned to the 10b vibration, then *Table 1* shows that few bands in this frequency range are now left unassigned. It must, therefore, be concluded that related bands in polystyrene derivatives are not observed. In no polymer is there any evidence of two vibrations, corresponding to coupling with different backbone configurations. Considering first poly(*p*-fluorostyrene), the band at 252 cm^{-1} is outside the range of the in-phase vibration 11, but may be the out-of-phase vibration 10b. The latter is expected to appear at a significantly higher frequency than the corresponding 10b vibration in polystyrene. The 212 cm^{-1} band for poly(*m*-fluorostyrene) may also be a 10b vibration with the frequency near to the upper limit of that range. In *ortho*-disubstitution, no Raman bands are observed at frequencies below those already assigned to 9a vibrations. The 10b vibration occurs at lower frequencies than in *meta*-disubstitution and may, therefore, overlap the 9a band. However, bands appearing at 295, 266 and 253 cm^{-1} in the *ortho*-isomers of polyfluorostyrene, polychlorostyrene and polybromostyrene are within the frequency range of the in-phase 10a vibration and may, possibly, be accordingly assigned. A Raman peak at 242 cm^{-1} for poly(*p*-bromostyrene) may be a 10b vibration, but there is no corresponding feature for the chlorine derivative. There is no band within this frequency range, apart from the 9a vibration, for poly(*m*-methylstyrene), and the 201 cm^{-1} band in poly(vinyl toluene) is therefore attributed to the *para*-substituted phenyl groups. The frequency is, however, anomalously low for an out-of-phase 10b vibration. The absence of any Raman band around 170 cm^{-1} for poly(α-methylstyrene) may not be significant, since the band at 168 cm^{-1} in polystyrene is very weak and the optical quality of the sample was much superior to that of the poly(α-methylstyrene) sample.

The evidence discussed above supports, albeit in a rather negative fashion, the assignment of the 168 cm^{-1} Raman band in polystyrene to a 10b vibration, and the bands tentatively assigned to vibrations 10a and 10b are connected by line I in *Table 1*.

It is clear from *Table 1* that several bands, particularly those in the region 300–400 cm^{-1} for *ortho*- and *para*-substituted samples, are left unassigned. Several other side-group vibrations are expected to occur within this frequency range, their activity depending, to a first approximation, on the local symmetry of the phenyl group[25]. Such assignments are relevant to the derivatives of polystyrene, but not to the Raman spectrum of polystyrene itself, and consequently assignments of these bands are not attempted here. The present work serves only as a test of previous polystyrene Raman band assignments[19].

It is not possible unambiguously to assign the neutron scattering in the region of 250 cm^{-1}. Contributions from the side-group vibrations discussed above and the maximum in the skeletal density of states are all likely to contribute.

The assignment of the 222 cm^{-1} Raman band for atactic polystyrene to a side-group vibration clearly affects the interpretation of lower frequency bands. The absence of any feature attributable to skeletal motion around 200 cm^{-1}, where the density of states shows a maximum[32], may imply that wave vector selection rules are operative. However the evidence is strong that the 20 cm^{-1} band is due to acoustic vibrations primarily involving skeletal motion and that the selection rules are therefore relaxed at this lower frequency. Why there should be such a difference is not clear, but may be connected with the different ratio of phonon wavelength to correlation length[1]. The alternative explanation for the absence of a skeletal peak at $\sim$200 cm^{-1}, namely that the chain model does not yield sufficiently accurate dispersion relations, is not appealing because any model is expected to yield a density of states peak at the zone edge and the energy must fall within the range 5–560 cm^{-1} we have studied. At this stage it is not possible to be definite about this intriguing point and we plan similar work on other amorphous systems which may help to understand the problem.

CONCLUSIONS

The Raman spectra of 'atactic' and partly crystalline isotactic polystyrene and some atactic derivatives of polystyrene are described covering the frequency range from 5 to 560 cm^{-1}. I.r. absorption data for the fluoro, chloro and bromo *para* substitutuents are also given over the same frequency range. The inelastic neutron scattering spectra have been measured up to 400 cm^{-1} for a variety of polystyrene related samples. The 20 cm^{-1} band in 'atactic' polystyrene was found to be insensitive to substitution of the phenyl group, although the 60 cm^{-1} band showed a decrease in intensity with increasing side-group mass and frequency shifts were also observed. A firm assignment of the latter feature is not possible on the basis of these measurements, but the results are interpreted as evidence for a motion of the phenyl group. Data for the 20 cm^{-1} band are consistent with the possibility that this is an acoustic vibration involving primarily skeletal motion. Indications of two Raman bands in the region of 60 cm^{-1} for samples of poly(α-methylstyrene) and isotactic, partially crystalline polystyrene are tentatively attributed to the influence of backbone chain conformations on side-group vibrations, in line with previous calculations[24].

No evidence was found for the existence of two C–X out-of-plane vibrations, corresponding to coupling with deformations of different backbone conformations, an effect which has recently been suggested[19]. Earlier Raman data on polystyrene appear to be unreliable in this frequency region. However, the same authors' assignments of bands at 410 and 216 cm^{-1} to an out-of-plane vibration of the phenyl group 'skeleton' and a C–X in-plane bending vibration[19] are supported by measurements on polystyrene derivatives, reported here. There is some indication that a very weak Raman band at 168 cm^{-1} in 'atactic' polystyrene may be due to a C–X out-of-plane vibration.

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