High-Resolution Incoherent Inelastic Neutron Scattering Spectra of Polyisobutylene and Polyisoprene

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ABSTRACT: High-resolution ($\Delta E/E \sim 2-3\%$) incoherent inelastic neutron scattering spectra of polyisobutylene and *cis*-1,4-polyisoprene have been obtained on the TFXA spectrometer at the ISIS pulsed neutron scattering facility. The observed bands are assigned with reference to available infrared and Raman data, and the differences observed are discussed. Particular emphasis is placed on the methyl group torsions which are not observable with the optical techniques. These bands are significantly broadened compared to the instrumental resolution, and this is attributed to a Gaussian distribution of local environment potentials for the methyl group, in agreement with present theoretical models. For polyisoprene, this assignment is confirmed by independent molecular dynamics simulations.

Introduction

Polyisobutylene (PIB) is one of the more unusual elastomeric polymers. It is known for several anomalous properties which are mostly dependent upon the low molecular mobility of the PIB backbone, e.g., its markedly low permeability to small-molecule penetrants and diffusants when compared to other elastomers.[1] As a consequence of the latter property it has found, as a copolymer with approximately 2% of *cis*-1,4-polyisoprene (PIP), natural rubber, a major commercial use in inner tubes and tire liners.

To exhibit elastomeric behavior, polymeric materials must have a dynamically mobile network.[2] This means in practice those materials which have a low glass transition temperature, T_g, and which do not crystallize under normal use conditions. Both PIB and PIP have regular structures, which makes crystallization possible, but their melting points are rather low (in the vicinity of room temperature); thus, the undercoolings required for crystallization are substantial, and in normal use they remain amorphous.

It has been suggested that low barriers to internal rotation about skeletal bonds are a contributing factor in maintaining the segmental mobility necessary for elastomeric behavior.[2] This may well be the case for PIP $(-CH_2-C(CH_3)=CH-CH_2-)_n$, but in PIB $(-C(CH_3)_2-CH_2-)_n$ the methyl groups bonded to alternate chain carbon atoms produce steric crowding. Although partially relieved by distortion of the $C-CH_2-C$ and CH_2-C-CH_2 bond angles (127° and 109°, respectively),[3] it is still significant and hence PIB is not very flexible. This might indicate that it is the relative simplicity of the chain cross section or surface which is an important parameter in determining elastomeric behavior and not just the presence, or otherwise, of side groups. Clearly information on the polymer dynamics whether it be of the whole chain or individual components such as the methyl groups is crucial in order to attempt to understand the reasons behind why PIB shows elastomeric character despite its apparent lack of flexibility.

Over the past three decades, neutron scattering techniques have contributed greatly to our understanding of polymer dynamics in general[4] and of methyl group dynamics in particular through studies of their relaxational behavior.[5] From these studies it is now accepted that in amorphous polymers there are distributions of relaxation times for methyl groups and therefore distributions of local environment potentials for the methyl groups. The assumption of a Gaussian distribution of the barriers to rotation gives a log−normal distribution of jump times of the protons.[5] This type of distribution has been confirmed by dielectric measurements (see ref 6 and references therein).

In this study we concentrate on obtaining a measure of the local environment potential for the methyl groups through vibrational spectroscopy. In general, methyl group torsions are not observable with optical techniques; hence, we have used incoherent inelastic neutron scattering (INS). On an appropriately designed spectrometer INS is the neutron scattering analogue to infrared and Raman vibrational spectroscopies. It offers a good resolution ($\Delta E/E \sim 2\%$) over a large energy-transfer range and has some important advantages over the optical techniques. First, there are no selection rules in INS, and in principle all bands can be observed. Second, in an INS spectrum the intensities of the normal modes of vibration are simply related to the amplitudes of the vibrations, making the comparison of data and ab initio calculations more straightforward.

Experimental Section

Samples. The PIB sample had an average molecular weight of 80 kg mol^{-1}. The PIP sample had a *cis*-1,4 content greater than 95%. The average molecular weight was 22 kg mol^{-1}. The sample size of both polymers used in the INS experiment was approximately 50 × 20 × 0.5 mm. For the measurements the samples were placed into an aluminum foil support attached

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to the end of a center stick suitable for insertion into a standard ISIS top-loading closed-cycle refrigerator.[7]

INS Measurements. The INS measurements were made on the time-focused crystal analyzer spectrometer, TFXA,[8] at the pulsed neutron scattering facility ISIS, CCLRC. This indirect geometry time-of-flight spectrometer has now been superseded by TOSCA,[9] which has an improved resolution and count rate.

Each sample was precooled to 77 K by immersion in liquid nitrogen before being placed into a cryostat and cooled to the measurement temperature of 25 K. A separate background measurement was also taken under the same experimental conditions.

Preliminary data reduction, converting from the raw time-of-flight data to the scattering law, $S(Q,\omega)$, and subtracting the background was carried out using standard programs.[10,11] In addition, although the sample sizes were nominally the same, the PIB spectrum was scaled to the PIP spectra by normalizing to the total scattering which simply entails integrating both spectra at high energies (where no features are present and the intensity observed is just proportional to the total scattering) to provide a scaling factor. The resolution function of TFXA is nominally Gaussian and varies as a function of energy transfer in a precisely known manner. Peak positions and widths were extracted by a Gaussian-fitting procedure within the open source software GNUPLOT with an imposed condition that the peak widths had to be not less than the width of the resolution function at the particular energy transfer value in question. The use of the Gaussian fitting procedure is justified on the grounds of the central limit theorem.

Results and Discussion

INS affords an insight into the dynamics of a system via the scattering law, $S(Q,\omega)$, which is related to the generalized vibrational density of states $G(\omega)$:

$$G(\omega) = \frac{S(Q,\omega)\omega}{Q^2(n(\omega) + 1)} \tag{1}$$

In the above equation, $Q = |\bar{Q}|$ is the modulus of the momentum transfer vector, ω is the vibrational frequency of an atom or a group of atoms, and $n(\omega)$ is the Bose factor.

Furthermore, if it is assumed that the majority of the scattering comes from the protons in the system (the incoherent scattering cross section of hydrogen is about 20 times greater than that of most other atoms) and the experiments are carried out at low temperature, then the scattering law can be expressed by[10]

$$S(Q,\omega_i) \approx \frac{1}{3}Q^2\sigma_{\mathrm{H}} \exp(-\gamma Q^2)\sum_n {}^n u_i^{\,2} \tag{2}$$

where ${}^n u_i^2$ is the mean-square displacement of atom n in mode i, σ_{H} is the incoherent cross section for a hydrogen atom, and Q is a function of u_i. The empirical parameter γ is an average mean-square amplitude of all motions for the hydrogen atoms. Since TFXA follows a specific trajectory through (Q,ω) space, it is worthwhile to recall the relationship between the momentum transfer Q and the energy ω: Denoting a wavevector of a neutron beam by $\bar{k}$, we have

$$\bar{Q} = \bar{k}_{\mathrm{inc}} - \bar{k}_{\mathrm{scatt}} \tag{3}$$

$$Q^2 = k_{\mathrm{inc}}^{\ 2} + k_{\mathrm{scatt}}^{\ 2} - 2k_{\mathrm{inc}}k_{\mathrm{scatt}}\cos(\theta) \tag{4}$$

The indices “inc” and “scatt” in the above equation refer to the incident and scattered neutron beam vector, respectively.

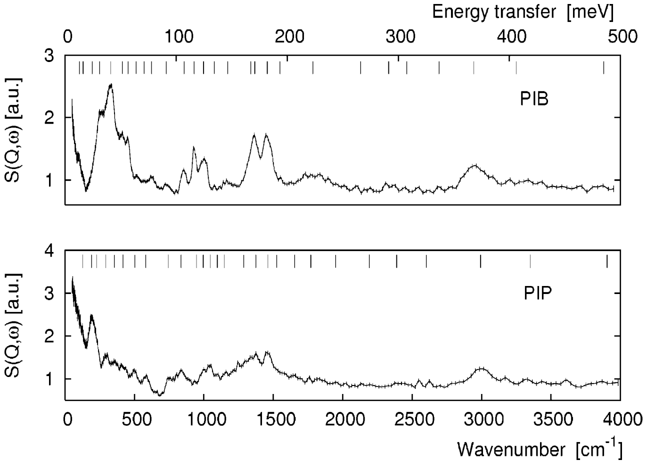

Figure 1. Full INS spectra of PIB and PIP.

Bearing in mind that the scattering angle θ is fixed at 135° and k_{scatt} is small, Q^2 can be approximated as $Q^2 = \omega/16.759$. By convention, the units are cm^{-1} for ω and Å^{-1} for Q. This approximation to Q^2 holds well above 200 cm^{-1}.

Polyisobutylene and Polyisoprene Spectra. The full INS spectra of PIB and PIP are shown in Figure 1. The markers indicate the positions of the fitted Gaussians. Full information regarding the peak positions and full widths at half-maximum (fwhm) from the Gaussian fitting procedure for PIB and PIP is shown in Tables 1 and 2, respectively.

It is customary to use fwhm ($= 2.354820045\sigma$) if there is only one well-defined frequency, and σ^2 is the variance of the assumed Gaussian distribution of frequencies. However, we felt that the choice of either convention is somewhat arbitrary in our case. The reason being that it is not possible to distinguish through model-free fitting how many functions contribute to a given feature if there is a combination of modes present.

Usually, information about distributions of activation energies is obtained from a measurement of relaxation rates as a function of temperature. A log−normal distribution of relaxation times follows naturally from an assumed normal distribution of activation energies,[5] but in order to extract distributions of activation energies unambiguously, one has to use simulations, e.g., molecular dynamics, as carried out recently for polyisobutylene.[13]

For discussion purposes the spectra can be split arbitrarily into three regions: a low-frequency region (50−800 cm^{-1}) which contains the methyl group torsions and backbone vibrations, a mid-frequency region (800−2600 cm^{-1}) containing various rocking and deformation vibrations involving the CH_2 and CH_3 groups, and the high-frequency region (2600−4000 cm^{-1}) containing the stretching vibrations. Where possible, the observed frequencies are compared to those obtained from infrared and Raman measurements. Note that the optical measurements were made at room temperature whereas the vibrational frequencies obtained from the INS measurements are made at 25 K and will usually be somewhat higher than the comparable optical frequencies.

Low-Frequency Region. In this region of the PIB spectrum there is a very intense structured band between 150 and 500 cm^{-1}. Both CH_3 torsions and

Table 1. Peak Positions and Assignment Scheme for Polyisobutylene*

freq ω/ $\mathrm{cm^{-1}}$	fwhm $\omega/\mathrm{cm^{-1}}$	resolution $\omega/\mathrm{cm^{-1}}$	assigment[a]	IR ω/ $\mathrm{cm^{-1}}$
105	25.5	8		
131	15.5	8		
197	46	8		
250	54	8.5	$\delta(\mathrm{C{-}C{-}C})$?	
330	74.5	9	$\tau(\mathrm{CH_3})^{0-1}$	
415	37	10	$\delta(\mathrm{C{-}C{-}C})$	
456	33	10	$\delta(\mathrm{C{-}C{-}C})$	
516	73	11	$\delta(\mathrm{C{-}C{-}C})$	510?
574	24	12		
627	62.5	13	$\tau(\mathrm{CH_3})^{0-2}$?	
735	60	15	$\gamma(\mathrm{CH_2})$?	
				829
863	45.5	18	$\gamma(\mathrm{CH_2})$	860?
				889
936	32.5	20	$\gamma(\mathrm{CH_3}) + \nu(\mathrm{C{-}CH_3}) + \delta(\mathrm{C{-}C{-}C})$	
				929
				953
1004	57	21.5	$\gamma(\mathrm{C{-}CH_3})^{0-1}$	1015
1084	15	24		1160
1180	107	27	$\gamma(\mathrm{CH_2}) + \tau(\mathrm{CH_3})^{0-1}$	
			mixed mode	1227
1349	86	32	$\mathrm{CH_3}$ bending doublet	1362
1378	44	33		1388
1467	36	36	? + $\delta_a(\mathrm{CH_3}) + \gamma(\mathrm{CH_2})$	
			$\delta_a(\mathrm{CH_3})$	1450
			$\delta(\mathrm{CH_2})$?	1463
1561	67	39		
1799	270.5	48	$\delta_a(\mathrm{CH_3}) + \tau(\mathrm{CH_3})^{0-1}$	
2145	215.5	62		
2351	75	71	$\gamma(\mathrm{C{-}CH_3})0-2 + \tau(\mathrm{CH_3})^{0-1}$?	
2481	216	76.5		
2715	19.2	87.5		
2970	150	100	$\nu(\mathrm{CH_2\ and\ CH_3}) + \gamma(\mathrm{C{-}CH_3})^{0-2} + \tau(\mathrm{CH_3})^{0-2}$?	
			$\nu_s(\mathrm{CH_2})$	2850
			$\nu_s(\mathrm{CH_3})$	2880
			$\nu_a(\mathrm{CH_2})$	2930
			$\nu_a(\mathrm{CH_3})$	2960
3277	623	115.5	$\nu(\mathrm{CH_2\ and\ CH_3}) + \tau(\mathrm{CH_3})^{0-1}$	
3912	215.5	150		

[a] Question mark indicates uncertain assignment.

backbone vibrations are expected to occur in this frequency range. A previous INS measurement of the vibrational density of states of PIB up to 800 $\mathrm{cm^{-1}}$ showed a structured band[14] centered at about 320 $\mathrm{cm^{-1}}$ which was assigned to be due to the $\mathrm{CH_3}$ group even though this is unusually high for a $\mathrm{CH_3}$ torsion. In PIP, for example, the $\mathrm{CH_3}$ torsion has previously been observed[15] at approximately 190 $\mathrm{cm^{-1}}$, and in this study a peak is also observed at 189 $\mathrm{cm^{-1}}$ (Figure 2). This rather high value for the $\mathrm{CH_3}$ torsion in PIB has been attributed to a strong coupling between the methyl groups which also may be related to the strong steric hindrance of the polymer chain in PIB.[16] In this study the approximate center of the band, as indicated by the position of the main Gaussian peak, is at 330 $\mathrm{cm^{-1}}$. Note that we measured at $T = 25$ K, whereas the measurements by Frick et al.[16] were carried out around the glass transition temperature, $T_g \approx 200$ K.

Regarding the structure in the PIB spectrum, there are some alternative explanations. The presence of two methyl groups on the same carbon atom can lead to coupled in-phase and antiphase vibrations of the $\mathrm{CH_3}$ groups which may also have an impact on the torsional frequencies and introduce structure into this region of the spectrum. However, it has already been stated that the amorphous nature of the polymer leads to a distribution of local potentials for the methyl groups, and this is more likely to produce a Gaussian broadening rather than extra structure. A simpler explanation would be that the structure is due to the fact that the C−C−C skeletal vibrations occur in the same region of the spectrum. These can be observed with reasonable intensity via the "riding motion" of the protons attached to the carbon atoms. This hypothesis is supported by comparing this spectrum with the spectrum of the PIP in which the lower frequency of the $\mathrm{CH_3}$ torsion removes it from the region of the backbone vibrations. Therefore, these features become much more obvious than in the PIB spectrum. The main peak at 330 $\mathrm{cm^{-1}}$ in PIB is quite broad (~88 $\mathrm{cm^{-1}}$; cf. the instrumental resolution of 9 $\mathrm{cm^{-1}}$). This extra width could then be ascribed to be the expected Gaussian broadening due to a distribution of local environment potentials for the $\mathrm{CH_3}$ groups in this amorphous polymer. It was not possible to resolve this into two or more components unambiguously. Selective deuteration of the polymer would resolve this issue as the incoherent scattering cross section of deuterium is much lower than that of hydrogen.

As is the case for PIB, the width of the torsional mode in PIP is again larger than the instrumental resolution, but not by so much (~41 $\mathrm{cm^{-1}}$ cf. 74.5 $\mathrm{cm^{-1}}$). In quasielastic neutron scattering studies of polyisoprene the dynamics of the methyl group were found to be strongly influenced by the heterogeneity of the local environment.[15] A distribution of the activation energies for 3-fold rotational jumps had to be assumed in order to interpret the observed spectra.

More quantitative insight into the nature of this broadening can be gained by calculating the generalized density of states $G(\omega)$ (eq 1) and comparison with the independent calculation of this quantity, as described in a section on comparison with the results of molecular dynamics simulations below.

The rest of the peaks in this region can be attributed to backbone vibrations or combination modes involving the intense $\mathrm{CH_3}$ torsional mode (see Tables 1 and 2). Most probably, the band at 627 $\mathrm{cm^{-1}}$ in PIB is the overtone of the $\mathrm{CH_3}$ torsion at 330 $\mathrm{cm^{-1}}$ rather than a backbone or combination mode. The fact that it occurs at less than twice the fundamental frequency is easily attributable to anharmonicity.

Mid-Frequency Region. PIB. In general, the $\mathrm{CH_2}$ rocking motion exists between 720 and 860 and $\mathrm{cm^{-1}}$. In aliphatic hydrocarbons which contain methylenic sequences of one, two, or three units, the frequency of the $\mathrm{CH_2}$ rocking band may be related to the number of hydrogens attached to the two carbon atoms bounding the sequence, and this concept can be extended to include polymeric systems.[17] In PIB it is calculated to be at 855 $\mathrm{cm^{-1}}$, and a band is observed in the infrared at 852 $\mathrm{cm^{-1}}$ along with two very weak features[18] at 829 and 889 $\mathrm{cm^{-1}}$. In the INS spectrum a band is seen at 863 $\mathrm{cm^{-1}}$ with a width of 45.5 $\mathrm{cm^{-1}}$, which again is larger than the instrumental resolution (18 $\mathrm{cm^{-1}}$ at this position) and so probably consists of more than one vibration. The most likely candidate is a combination mode involving the $\mathrm{CH_3}$ torsion and the skeletal vibration at 516 $\mathrm{cm^{-1}}$ ($330 + 516 = 846$ $\mathrm{cm^{-1}}$).

The second band in this region at 936 $\mathrm{cm^{-1}}$ is sharper and more intense and is attributable to a coupled vibration. In the IR spectrum of PIB there is a doublet at 923 and 950 $\mathrm{cm^{-1}}$ arising from a coupled vibration

Table 2. Peak Positions and Assignment Scheme for Polyisoprene[a]

fitted line position ω/cm^{-1}	fwhm ω/cm^{-1}	TFXA resolution ω /cm^{-1}	IR ω/cm^{-1}	assignment IR	R^1 ω/cm^{-1}	assignment Raman	R^2 ω/cm^{-1}
126	4.5	8					
189	35	8			179		
225	40	8.5					
295	50	9					
353	45	9			343		
					355	$\gamma_s(=CC_2)$	
		10					
418	76	10			428	$\gamma_r(=CC_2)$	
		10					
							471
502		11			493	$\gamma_r(=CC_2)$, $\gamma_s(=CC_2)$	496
581	58	12			565		565
744	34	15	742	? of $C(CH_3)=CH-$	728		
			762				
		17			816		
833 or 837	110 or 96	17.5	840	$\delta(CH)_{op}$ of $C(CH_3)=CH-$			
			845	trans			
			870	crystallinity band			
			890	$\delta(CH)_{op}$ of isopropanyl	889	δ (CH)	870−890
947	76	20	931				
995	42	21.5	980	$\nu(C-CH_3)$	996		
			1013	$\nu(C-CH_2)$			
1045	43	23	1040	$\gamma_r(CH_3)$	1038	$\gamma_r(CH_3)$	
					1070	?	
1096	30	24	1105	$\nu(C-CH_2)$			
?	?	?	1130	$\nu(C-CH_3)$	1130	$\nu(C-CH_3)$	
1147	38	26	1152	trans			
			1212		1201		
		29	1245	$\gamma_t(CH_2)$	1238		
1287	212	30	1294	$\delta(CH)_{ip}$	1286		1287
		32	1315	$\nu(=C-H)$ of $C(CH_3)=CH-$	1308	$\delta(=CH)_{ip}$?	1312
			1325	trans	1321	$\delta(=CH)_{ip}$?	1326
			1361	CH_2	1359	$\gamma_w(CH_2)$	1364
					1369	$\delta_s(CH_3)$	1375
1374	67	33	1380	$\delta_s(CH_3)$			
					1431	δ (CH_2)	
1460	49	36	1450	$\delta_{as}(CH_3)$	1445	$\delta_a(CH_3)$	
1525	129	38					
		40					
			1645	$\nu(C=C)$ of isopropenyl			
1655	47	42.5	1665	$\nu(C=C)$ of $C(CH_3)=CH-$	1662	$\nu(C=C)$ of $C(CH_3)=CH-$	
1771	495	47					
		50					
1949	225	54					
2192	156	64					
2388	116	72.5					
2602	360	82					
			2717		2724		
			2833	$\nu_{as}(CH_2)$	2853		
			2890	$\nu_s(CH_3)$	2878	$\nu_s(CH_3)$	
			2907	$\nu_s(CH_2)$	2910		
			2924	$\nu_{as}(CH_3)$	2929	$\nu_i(CH_2)$	
					2957	$\nu_a(CH_3)$	
2992	204	101	3000	$\nu(=CH)$ of $C(CH_3)=CH-$			
					3033	$\nu(=CH)$ of $(C(CH_3)=CH-)$	
			3077	$\nu(=CH)$ of isopropenyl			
3352	395	119.5					
3610	58	133.5					
3903	316	150					

[a] Question mark indicates uncertain assignment.

involving the CH_3 rock and C−C stretch.[19] This correlates well with the peak position in the INS spectrum (the doublet is unresolved).

The third rather intense band at 1004 cm^{-1} (fwhm = 57 cm^{-1}) has weak counterparts in the infrared spectrum[18] at 984 and 1017 cm^{-1}. Its intensity in the INS would suggest that it is a fundamental vibration involving significant proton motion. The most likely candidate would be the CH_3 rocking vibration, especially when it is considered that such a vibration may be split due to the two methyl groups vibrating in-phase and out-of-phase with each other.

There is some intensity at 1180 cm^{-1} which could correspond to a combination mode involving the CH_3 torsion and CH_2 rock. There is a corresponding band in the infrared[18] at 1160 cm^{-1}.

In the infrared spectrum there is a strong peak at 1230 cm^{-1} which has been attributed to a coupled

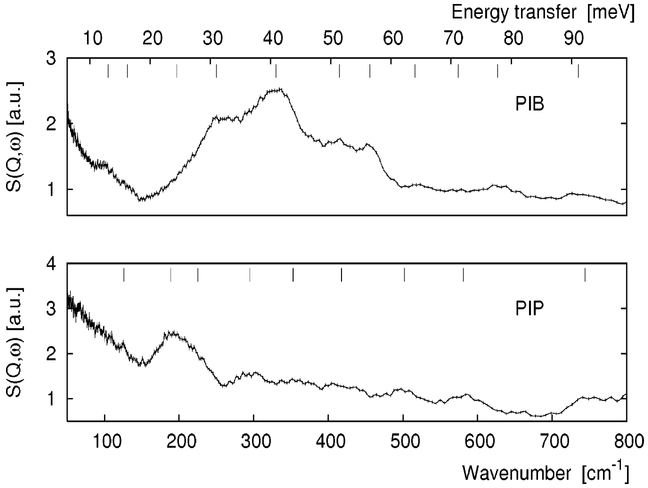

Figure 2. Low-frequency regions of the polyisobutylene (PIB) and polyisoprene (PIP) IINS spectra.

vibration involving C−C stretching, both of the polymer backbone and of the bond joining the methyl group to the backbone, together with C−H bending and CH_3 rocking vibrations.[19] In the INS spectrum no feature is present. This must cast some doubt on its assignment as a vibration involving significant proton motion (CH bend and CH_3 rock). It is unlikely at the low temperature of our measurement that the frequency of this band has changed by the 70−80 cm^{-1} necessary to move it into the region of the next intense vibration. Similarly, it is also unlikely that the frequency has *dropped* sufficiently (as have some of the other mode frequencies) to put it into the band at 1180 cm^{-1}.

Next come two very intense peaks centered at 1378 and 1467 cm^{-1} with a broader peak underlying them at 1349 cm^{-1}. In PIB an important diagnostic feature in the infrared spectrum is the CH_3 symmetric deformation doublet at 1365 and 1388 cm^{-1} which is characteristic of two methyl groups attached to a single carbon atom.[19] This splitting is due to H···H steric repulsion. There is also an obvious combination mode involving the CH_3 torsion and the CH_3 rock (330 cm^{-1} + 1004 cm^{-1} = 1334 cm^{-1}). Furthermore, the CH_2 wag and twist vibrations occur[20] at 1275 ± 100 and 1300 ± 5 cm^{-1}. A lack of interaction with any of the other methylene groups would mean that these frequencies will be toward the high-frequency end of these ranges and so would fall quite naturally into the band centered at 1378 cm^{-1}. Therefore, these bands would account for the first peak.

Interestingly, there is no evidence for a combination band at ∼1250 cm^{-1} which would be expected if the low-frequency feature in the region of the methyl group torsions at ∼240 cm^{-1} is itself a torsion. This provides further evidence that the methyl torsional frequency is indeed at 330 cm^{-1}.

The assignment of the peak at 1467 cm^{-1} is a little more complicated. CH_3 deformation vibrations are sensitive to the electronegativity of the attached atoms and for the case of $C-CH_3$ the frequency of the asymmetric deformation, $\delta_{as}(CH_3)$, can be calculated[20] (pp 222−225):

$$\delta_{as}(CH_3) = 0.25\delta_s(\mathrm{CH_3}) + 1105 \tag{5}$$

Taking an average value of 1375 cm^{-1} for the symmetric deformation would put the CH_3 asymmetric deformation at around 1450 cm^{-1}. Furthermore, the CH_2 scissors deformation is normally located in the mid-1400's, e.g., at 1463 ± 13 cm^{-1} in long-chain alkanes. In the infrared spectrum there is an intense asymmetric band which does include a component at around 1450 cm^{-1} and certainly includes an unresolved doublet at 1470 and 1480 cm^{-1}. Therefore, we assign the band in the INS spectrum at 1467 cm^{-1} to consist of the asymmetric deformation of the CH_3 group along with the CH_2 scissors mode.

Finally, there is a broad (270.5 cm^{-1}) band at around 1800 cm^{-1} in the INS spectrum. This is a combination of the bands discussed above with the CH_3 torsion.

Mid-Frequency Region. PIP. For PIP an early assignment of bands in the infrared at 742 and 762 cm^{-1} as being due to the CH_2 rock was deemed unlikely, and an alternative assignment as some unspecified vibration of the $C(CH_3){=}CH$ group was suggested.[21] Using the same argument as above for PIB, the CH_2 rock should occur at around 750−760 cm^{-1}. Furthermore, a normal-coordinate analysis of semicrystalline *trans*-1,4-polyisoprene puts the CH_2 rock at 752 or 758 cm^{-1} depending upon the crystalline form.[22] Therefore, we assign the band at 744 cm^{-1} in the INS spectrum to be due to the CH_2 rock.

Other identifying bands for PIP are at 816 and 889 cm^{-1} (corresponding to the CH rock) and at 1130 cm^{-1} (assigned to be a vibration of the $C-CH_3$ group). In the INS spectrum there are bands at 833, 1014, and 1045 cm^{-1}. The lower frequency band could be the unresolved 816 and 889 cm^{-1} bands. The bands at 1014 and 1045 cm^{-1} are more likely to be associated with the CH_3 rock vibration which occurs in a similar position in the PIB spectrum.

The peak at 1374 cm^{-1} is most easily assigned to be the CH_3 symmetric deformation particularly as formula 5 gives the value of 1448 cm^{-1} for the asymmetric deformation which agrees well with the observed peak at 1463 cm^{-1}.

In the Raman spectrum of PIP there is a very strong band at 1660 cm^{-1} assigned to be the C=C stretch.[23] This is not observed in the INS spectrum.

This region contains the stretching vibrations. There are four bands expected: the CH_2 and CH_3 symmetric and asymmetric stretches. Aliphatic CH_2 and CH_3 groups give rise to doublets separated by approximately 80 cm^{-1}, i.e., 2880 and 2960 cm^{-1} for CH_3 and 2850 and 2930 cm^{-1} for the CH_2 bond;[20] the symmetric and antisymmetric stretching modes at 2880 and 2960 cm^{-1}. In the INS spectra the lower resolution in this region (100 cm^{-1}) means that there is just a single band observed centered at 2970 cm^{-1} which covers all of the C−H stretching vibrations.

Comparison with Results of Molecular Dynamics Simulation. We have calculated the generalized vibrational density of states function $G(\omega)$ (eq 1) in order to compare our results with these obtained by others. Figures 4 and 5 show $G(\omega)$ for polyisobutylene (PIB) and polyisoprene (PIP), respectively.

First, a flat background is subtracted from data since the incoherent scattering is isotropic *unless* there is inelastic scattering. The latter would depend on the momentum transfer Q and temperature through the Debye−Waller factor (DWF). We assume that the real spectra, $S_{obs}(Q,\omega)$), are described by the formula

$$S_{obs}(Q,\omega) = \exp(-2W)S(Q,\omega) \tag{6}$$

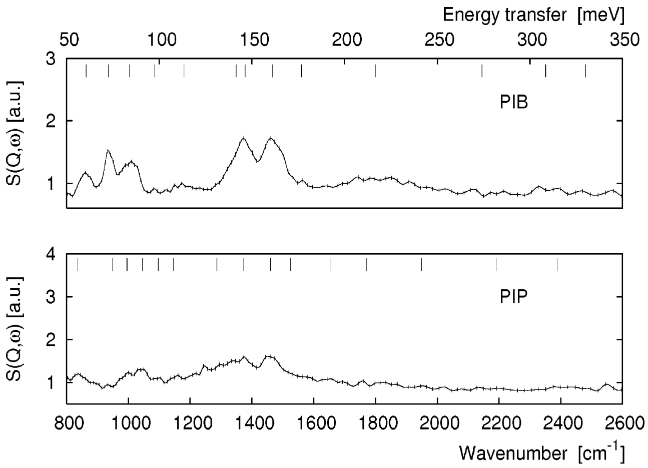

Figure 3. Middle-frequency regions of the PIB and PIP IINS spectra.

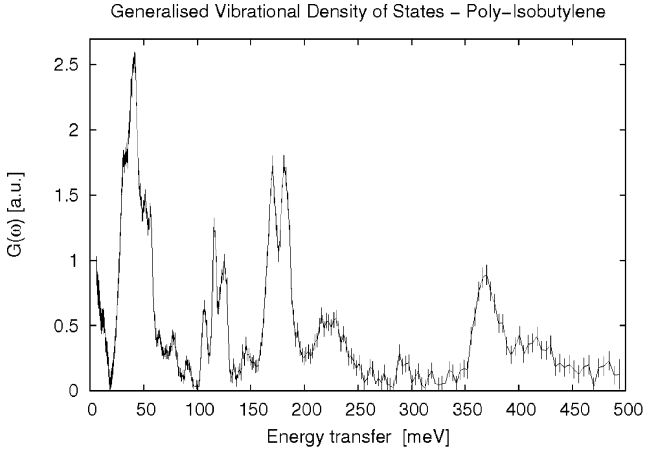

Figure 4. Generalized vibrational density of states $G(\omega)$ calculated according to eq 1 for polyisobutylene (PIB).

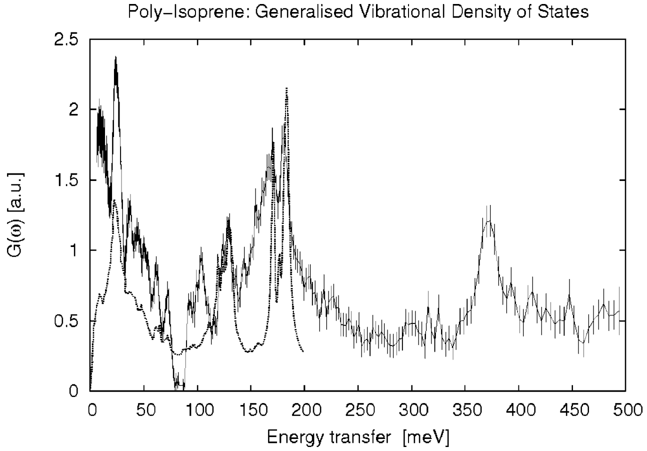

Figure 5. Comparison of $G(\omega)$ measured by us (solid line) with that calculated[24] for the methyl group from MD simulations. The dip in the measured $G(\omega)$ is an instrumental artifact.

where W is the Debye–Waller factor, $W = \exp(-u^2Q^2)$, with u^2 being the mean-square displacement. The least-squares fit is then carried out with the averaged value of the DWF. The resulting generalized density of states function $G(w)$ for PIB is shown in Figure 4. To best of our knowledge, there are no molecular dynamics or other simulations for $G(\omega)$ for polyisobutylene. However, the methyl group dynamics in this polymer has been simulated by Karatasos et al.,[13] and results were compared to the ^{13}C NMR and NMR data. The authors concluded that the methyl group motion is strongly coupled with backbone motion. This coupling persists even to low temperatures, resulting in a process which cannot be described in terms of 3-fold rotation only.

Figure 5 shows a comparison of the vibrational density of states measured by us with the vibrational density of states calculated for the methyl group protons in polyisoprene by Alvarez et al. Their simulation stops at 200 meV. This simulation aids our assignment of the observed frequencies to methyl groups and chain vibrations, respectively. While there is a very good agreement between their simulations and our measured spectrum in the region 25–200 meV, three strong features are not reproduced in calculations. First is a strong upturn toward the elastic peak, which can be interpreted as a mixture of the elastic shoulder, diffraction lines, and possibly a tail of a boson peak.[16] Other assignments in this region are listed in Table 2 and were discussed above.

The model used by Alvarez et al.[24] concerns methyl group dynamics only and has two assumptions: the methyl group rotation has to be described in terms of 3-fold potential with an addition of a small 6-fold term, and there is a distribution of barriers to rotation. The authors achieve excellent agreement with neutron data (see Figure 5 in their paper) in the energy range 0–40 meV (about 320 cm^{-1}). The predicted features in the region above this correspond well in the main to our spectrum; however, the broadening of several peaks remains not accounted for.

Conclusions

We have measured and analyzed the high-resolution INS spectra of polyisobutylene and polyisoprene and compared the resulting frequencies with the IR and Raman data where available. Some of the frequencies have been measured for the first time. In the low-frequency region, we were able to confirm the existence of complicated distributions of torsional frequencies of the methyl groups in both polymers. While it was straightforward to identify the CH_3 torsion in PIP at 189 cm^{-1}, in agreement with previous literature data,[15] the case of PIB is more complex. The existing assignment of the frequency centered at 330 cm^{-1} as due to a strong coupling between two methyl groups[14,16] seems less plausible in light of our measurements. Another possibility would be to assume even more complex mechanism involving rotation rate distribution model and tunneling of methyl groups, as proposed for poly(methyl methacrylate) (PMMA).[25] We propose that the peak at 330 cm^{-1} is due to a broadened methyl group torsional frequency, and the structure is due mainly to the C–C–C skeletal vibrations being in the same region of the spectrum. A quantitative confirmation of this hypothesis will be the scope of future work since it requires a calculation of the full vibrational spectrum.

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